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LOS ANGELES FIELD MODELING AND MEASUREMENT STUDY - 1976

First Year Final Report

by

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In October 1976 a two-week field program was conducted in Los Angeles to evaluate in the field existing measurement methods for ambient concentrations of sulfuric acid aerosol and related sulfates, and to obtain preliminary data for the in-roadway concentrations of sulfates due to catalyst equipped vehicles. Participating organizations included Caltech, Univ. of Minnesota, Washington Univ., Rockwell International, and the EPA. The in-roadway increments of sulfate were small enough to scatter around zero on all days, and were smaller than 2 $\mu g/m^3$. About 30% of the automobiles on the freeways were equipped with catalysts at this time. Sulfuric acid was not detected in normal freeway traffic, but it is believed that measures used to protect it from neutralization during sampling were not adequate. Ambient ammonia concentrations were much greater than required to neutralize the possible in-roadway sulfuric acid on all days. Physical aerosol measurements gave a grand average increment of 9.8 $\mu m^3/cm^3$ in the nuclei mode size range, and 21 $\mu m^3/cm^3$ in the accumulation mode. Lead concentration increments in the nuclei mode size range were as great as 10 $\mu g/m^3$. Scatter diagrams show that the in-roadway increments of NO_x, CO, SO_2 and several aerosol physical parameters do not correlate well. The statistical design of an in-roadway sampling program to determine distribution functions for the exposure of the Los Angeles population to elevated concentrations of vehicle exhaust pollutants is described.

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ABSTRACT

In October 1976 a two-week field program was conducted in Los Angeles to evaluate, in the field, existing measurement methods for ambient concentrations of sulfuric acid aerosol and related sulfates, and to obtain preliminary data for the in-roadway concentrations of sulfates due to catalyst equipped vehicles. Participating organizations included Caltech, University of Minnesota, Washington University, Rockwell International, and the EPA. The in-roadway increments of sulfate were small enough to scatter around zero on all days, and were smaller than 2 ug/m^3. About 30% of the automobiles on the freeways were equipped with catalysts at this time. Sulfuric acid was not detected in normal freeway traffic, but it is believed that measures used to protect it from neutralization during sampling were not adequate. Ambient ammonia concentrations were much greater than required to neutralize the possible in-roadway sulfuric acid on all days. Physical aerosol measurements gave a grand average increment of 9.8 um^3/cm^3 in the nuclei mode size range, and 21 um^3/cm^3 in the accumulation mode. Lead concentration increments in the nuclei mode size range were as great as 10 ug/m^3. Scatter diagrams show that the in-roadway increments of NOx, CO, SO_2 and several aerosol physical parameters do not correlate well. The statistical design of an in-roadway sampling program to determine distribution functions for the exposure of the Los Angeles population to elevated concentrations of vehicle exhaust pollutants is described. Care was taken to make the design experimentally efficient, and free of the use of atmospheric dispersion models or assumptions about the mathematical form of the distribution functions.

This report was submitted in fulfillment of Contract 68-02-2463 by Rockwell International Environmental Monitoring and Services Center (EMSC), under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from September 1976 to February 1979, and work was completed as of December 1980.

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We are also grateful for the cooperation and support provided by R. K. Stevens, the Project Officer.

1.0 INTRODUCTION

In order to meet the requirements of the Clean Air Act, vehicle manufacturers began using catalytic converters in automobiles in the 1975 model year. These devices have the objective of oxidizing the emitted hydrocarbons and carbon monoxide, but workers at Ford (Pierson, Hammerle, and Kummer, 1974) discovered that they have the side result of oxidizing some of the sulfur in the fuel to sulfuric acid. When this became known many people became concerned that these emissions would lead to unhealthy, or even dangerous, concentrations of sulfuric acid on roadways. Early work on this problem has been reviewed by Bradow and Moran (1975).

1.1 PRIOR FIELD STUDIES

As soon as it became known that catalyst equipped cars emit sulfuric acid, the EPA began making plans for a field study to obtain data to determine the importance of this problem. Because of the greater sulfuric acid emission rate of cars with California emission control equipment and the high densities of traffic which occur on the freeways in Los Angeles, the study was initiated in that city, and has become known as the Los Angeles Catalyst Study (U. S. EPA, 1974). Data are being taken at a series of fixed sites which lie on a line perpendicular to the San Diego Freeway near Wilshire Blvd. This site was picked because traffic counts approach 200,000 cars per day, the site is relatively free from the impact of the emissions from stationary sources, the prevailing wind is perpendicular to the roadway, the freeway elevation is near grade, and adequate space and utilities were available. Data collection began at about the same time the first catalyst equipped cars began to appear on the roadway. At the time the work reported below was undertaken, the best estimates of the contribution of the San Diego Freeway to the sulfate concentrations at the downwind side of the freeway were about 5 ug/m^3.

Shortly before the work reported here was carried out, the General Motors Sulfate Dispersion Experiment was conducted at the Milford Proving Grounds (Cadle, Chock, Heuss, and Monson, 1976; Stevens, et al., 1976; Cadle, Chock, Monson, and Heuss, 1977; Wilson et al., 1977). This experiment showed that the buildup of pollutants on and near roadways during stagnant meteorological conditions is limited by the turbulence and heat generated by vehicles, and that the concentration gradient of the emissions in the vicinity of the roadway is great enough that the population primarily at risk is the vehicle occupants.

These results and an unpublished analysis by Papetti and Horowitz led to the development of A second EPA-sponsored study of sulfates in roadways in the Los Angeles area and the results of the first year of that study are contained in this report. The distinctive features of this study are that the measurements are made within the roadway so that no modeling or transformation of the data are required to obtain the concentrations of sulfates to which the population primarily at risk is exposed. The results from this study were first released at a conference sponsored by the Catalyst Research Program of the EPA held at the Kanuga Conference Center, Hendersonville, NC, on 31 January through 3 February, 1977 (Health Effects Research Laboratory, 1977).

1.2 OBJECTIVES OF THIS STUDY

The purposes of the first year of the Los Angeles Field Modeling and Measurement Study are to evaluate in the field methods for measuring sulfuric acid and related sulfates on roadways, and to design a field sampling program which will determine the exposure of the vehicle occupants in Los Angeles to sulfates from catalyst equipped vehicles.

The initial activity of the Environmental Monitoring & Services Center (EMSC), Rockwell International under the program was to support a field program conducted by the EPA, the University of Minnesota, Washington University, and Caltech during the last two weeks of October, 1976. The major EMSC responsibilities related to this contract were to operate the sulfuric acid monitor and to provide wet chemical analyses. Also this Final Report, containing the results obtained by all of the cooperating investigators during the first year of the study, was to be prepared.

2.0 DATA FROM THE OCTOBER 1976 FIELD PROGRAM

This section contains a description of the experimental program and a summary of the data obtained. The interpretation of these data is given in Section 3.0 along with a discussion of the conclusions which can be drawn. A description of the design of the program planned to follow the one reported here is given in Section 4.0.

2.1 OVERVIEW OF THE FIELD PROGRAM

The chief objectives of the field program were to implement in the field and evaluate new measurement methods for pollutants emitted from vehicles, especially catalyst equipped automobiles, and to obtain information on the concentrations of these pollutants on the freeways during the time of the experiments. A number of measurement techniques and new instruments were used in the field for the first time in this study, and several of them gave promising results.

A general plan of the field experiment was to use three vehicles as mobile laboratories to make measurements on the roadways and nearby background sites. Caltech operated a van which remained at a background site upwind of the freeway used for the in-roadway measurements and took data at the same time the other two vehicles were on the freeway. The University of Minnesota and Washington University operated a van and a car, respectively, and made measurements alternately on a 10 or 15 mile long section of the freeway and then beside the Caltech van at the background site. Figure 1 is a map showing the location of the freeway segments on which measurements were made as well as the sites for the background measurements. On most days, measurements were made either during and shortly after the morning rush hour, or in the afternoon. A few special experiments were performed, such as making a series of measurements at varying downwind distances from a freeway in a region otherwise relatively free of pollution sources. On the last day of the program, 30 October, measurements were made from 0317 to 0622 in the early morning behind seven catalyst equipped cars on the Foothill Freeway, Interstate 210.

2.2 THE CALTECH DATA

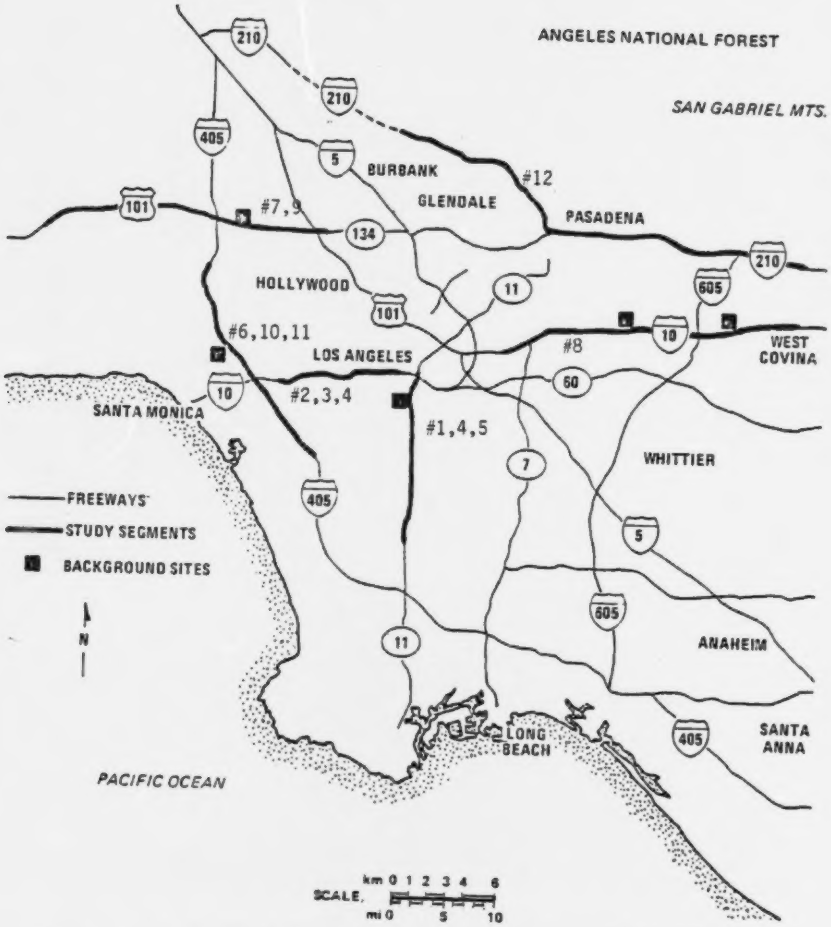

ANGELES NATIONAL FOREST
SAN GABRIEL MTS.
210
210
405
5
BURBANK
#12
101
#7,9
GLENDALE
PASADENA
134
210
HOLLYWOOD
11
605
101
#6,10,11
10
WEST COVINA
LOS ANGELES
#8
60
10
SANTA MONICA
#2,3,4
#1,4,5
WHITTIER
7
FREEWAYS
STUDY SEGMENTS
BACKGROUND SITES
405
5
N
605
11
ANAHEIM
LONG BEACH
405
SANTA ANNA
PACIFIC OCEAN
SCALE, km 0 1 2 3 4 6
mi 0 5 10

Figure 1. Locations of the Freeway Segments and Background Sites Where Measurements Were Made. The University of Minnesota Run Numbers are Indicated.

The group from the California Institute of Technology which participated in this study was associated with Professor S. K. Friedlander. The work was primarily organized and led by Dr. Susanne Hering. Caltech served as the host for this study, and provided those innumerable services and amenities that make such a field program fruitful. Caltech also operated a van which made measurements at the background site selected for each day. The instruments that were in the van are listed in Table 1, along with the name of the organization responsible for supplying the instrument or for analyzing the filter aerosol samples which it collected.

Table 1. Instruments in the Caltech Van

Manual Dichotomous Sampler (Caltech - EMSC)
Low Pressure Impactor (Caltech)
TWOMASS Sampler (Washington University)
Ammonia Sampler (EMSC)
Meteorological Measurements (Caltech)

The low pressure impactor (LPI) used by Caltech is a single-jet, eight-stage impactor with 50% collection efficiency cut sizes of 0.050, 0.075, 0.12, 0.26, 0.5, 1.0, 2.0 and 4.0 um aerodynamic diameter (Hering, Flagan and Friedlander, 1978; Hering, Friedlander, Collins, and Richards, 1979). This impactor is especially suited for analysis of aerosol sulfur by the method of flash volatilization and flame photometric detection. Particles larger than 0.5 um are size segregated and collected using the first four stages of the Battelle impactor. Four additional stages, operating at pressures of 8 to 150 Torr absolute, size segregate and collect the smaller particles. The collection efficiency of stages 4 through 6 have been calibrated with polystyrene latex spheres (Hering, et al., 1978), and the efficiencies of stages 7 and 8 have been calibrated with monodisperse uranine aerosols (Hering, et al., 1979). The impaction surfaces are coated with vaseline to minimize particle bounce-off and re-entrainment. Comparisons between the LPI and an Electrical Aerosol Analyzer using laboratory-generated ammonium sulfate and sulfuric acid aerosols gave good agreement.

The data from the low pressure impactors in the Catech van and the University of Minnesota van are summarized in Tables 2 and 3. Sulfur data from each stage of the impactor are available, but only the total aerosol sulfur data are given in Table 2, and the aerosol sulfur in particles smaller than 0.12 um are reported in Table 3. The latter numbers are the sum of the results obtained from impactor stages 7 and 8.

Table 2. Total Aerosol Sulfur Concentrations Obtained by Summing the Data for Stages 1 Through 8 of the Low Pressure Impactor

	U. Minn. Van LPI				Caltech Van LPI		
Date	Sample #	Time	Location[*]	μg/m^3 S	Sample #	Time	μg/m^3 S
10-19-76	1M	15:08-16:01	F	3.09±0.28	1C	15:07-15:48	5.88±0.53
	2M	17:16-17:51	B	2.85±0.26	2C	17:16-17:54	4.97±0.45
	3M	Return trip	F	3.36±0.30			
10-20-76	4M	14:55-15:25	F	4.26±0.51			
	5M	15:43-16:13	F	3.83±0.45	3C	15:36-16:45	4.74±0.47
	6M	16:35-17:05	B	2.65±0.35			
	7M	17:30-18:05	F	2.74±0.32	4C	17:26-18:25	4.57±0.46
	8M	18:52-19:22	B	2.74±0.37	5C	18:45-19:13	3.82±0.48
10-21-76	9M	07:55-08:35	F	2.05±0.22	6C	07:50-08:29	2.61±0.25
	10M	09:50-10:25	F	2.36±0.24	7C	09:42-10:30	2.35±0.22
	11M	10:45-11:15	B	2.31±0.26	8C	10:45-11:15	2.27±0.26
10-22-76	12M	08:14-07:23	F	1.92±0.18	9C	07:17-08:16	2.51±0.21
	13M	09:10-09:40	F	1.96±0.24	10C	09:01-10:00	2.15±0.18
	14M	10:12-10:37	B	1.81±0.25	11C	10:12-10:42	2.19±0.24
10-24-76	15M	15:30-15:40	F	1.40±0.19	12C	15:15-15:54	1.97±0.22
	16M	16:10-16:40	B	2.70±0.31	13C	16:15-16:40	3.33±0.39
	17M	17:04-17:34	F	2.35±0.30	14C	16:58-17:38	2.96±0.30
10-25-76	18M	15:03-15:30	F	2.92±0.35			
	19M	16:30-17:00	F	2.17±0.27	15C	16:10-17:16	3.15±0.31
	20M	18:05-18:40	F	2.15±0.27	16C	18:00-18:54	2.41±0.25
	21M	19:00-19:30	B	1.84±0.25	17C	19:07-19:37	2.58±0.31
	22M	20:00-20:20	F	1.68±0.27			
10-26-76	23M	15:00-16:00	F	0.27±0.06	18C	14:30-16:13	0.31±0.05
	24M	16:28-17:13	B	0.38±0.09	19C	16:28-17:12	0.45±0.12
	25M	17:20-18:20	F	0.27±0.06	20C	17:20-18:10	>0.22
10-27-76	26M	07:00-08:00	F	0.75±0.11	21C	06:56-07:56	0.81±0.13
	27M	08:35-09:30	F	1.20±0.15	22C	09:11-09:39	1.37±0.24
	28M	09:45-10:33	B	0.79±0.13	23C	09:47-10:32	0.86±0.14
	29M	14:00-15:05	F	0.53±0.08	24C	14:43-15:07	0.83±0.21
	30M	15:20-16:20	B	0.33±0.07	25C	15:21-16:22	0.60±0.09
	31M	16:40-17:35	F	0.59±0.08	26C	16:42-17:27	1.00±0.13
10-28-76	32M	16:16-17:17	B	0.93±0.11	27C	16:05-16:55	1.05±0.13
	33M	17:40-18:42	F	1.38±0.13	28C	17:34-18:19	>1.68±0.16
10-30-76	34M	03:17-03:33	B	0.86±0.10	29C	03:14-04:32	1.16±0.13
	35M	05:22-06:22	F	0.73±0.10	30C	05:17-06:26	1.27±0.15

[*] F = in freeway
B = background site

Table 3. Aerosol Sulfur Concentrations in Particles Smaller Than 0.12 μm Calculated (Without Correction) from Stages 7 and 8 of the Low Pressure Impactor

	U. Minn. Van LPI				Caltech Van LPI		
Date	Sample #	Time	Location*	$\mu g/m^3$ S	Sample #	Time	$\mu g/m^3$ S
10-19-76	1M	15:08-16:01	F	0.24±0.02	1C	15:07-15:48	0.25±0.01
	2M	17:16-17:51	B	0.22±0.02	2C	17:16-17:54	0.29±0.03
	3M	Return trip	F	0.24±0.02			
10-20-76	4M	14:55-15:25	F	0.50±0.08			
	5M	15:43-16:13	F	0.47±0.07	3C	15:36-16:45	0.35±0.05
	6M	16:35-17:05	B	0.30±0.06			
	7M	17:30-18:05	F	0.18±0.06	4C	17:26-18:25	0.26±0.03
	8M	18:52-19:22	B	0.35±0.07	5C	18:45-19:13	0.28±0.06
10-21-76	9M	07:55-08:35	F	0.27±0.04	6C	07:50-08:29	0.26±0.04
	10M	09:50-10:25	F	0.30±0.04	7C	09:42-10:30	0.15±0.03
	11M	10:45-11:15	B	0.16±0.04	8C	10:45-11:15	0.19±0.04
10-22-76	12M	08:14-07:23	F	0.34±0.03	9C	07:17-08:16	0.11±0.02
	13M	09:10-09:40	F	0.21±0.04	10C	09:01-10:00	0.11±0.02
	14M	10:12-10:37	B	0.15±0.02	11C	10:12-10:42	0.20±0.05
10-24-76	15M	15:30-15:40	F	0.20±0.04	12C	15:15-15:54	0.25±0.03
	16M	16:10-16:40	B	0.18±0.04	13C	16:15-16:40	0.22±0.06
	17M	17:04-17:34	F	0.28±0.05	14C	16:58-17:38	0.11±0.03
10-25-76	18M	15:03-15:30	F	0.49±0.07			
	19M	16:30-17:00	F	0.24±0.04	15C	16:10-17:16	0.18±0.03
	20M	18:05-18:40	F	0.32±0.05	16C	18:00-18:54	0.20±0.03
	21M	19:00-19:30	B	0.18±0.04	17C	19:07-19:37	0.20±0.04
	22M	20:00-20:20	F	0.18±0.05			
10-26-76	23M	15:00-16:00	F	0.12±0.02	18C	14:30-16:13	0.08±0.01
	24M	16:28-17:13	B	0.06±0.02	19C	16:28-17:12	0.06±0.01
	25M	17:20-18:20	F	0.10±0.02	20C	17:20-18:10	-0.01±0.01
10-27-76	26M	07:00-08:00	F	0.35±0.04	21C	06:56-07:56	0.25±0.03
	27M	08:35-09:30	F	0.60±0.06	22C	09:11-09:39	0.62±0.08
	28M	09:45-10:33	B	0.36±0.04	23C	09:47-10:32	0.29±0.04
	29M	14:00-15:05	F	0.18±0.02	24C	14:43-15:07	0.26±0.06
	30M	15:20-16:20	B	0.14±0.02	25C	15:21-16:22	0.07±0.02
	31M	16:40-17:35	F	0.18±0.02	26C	16:42-17:27	0.16±0.03
10-28-76	32M	16:16-17:17	B	0.19±0.01	27C	16:05-16:55	0.20±0.03
	33M	17:40-18:42	F	0.80±0.05	28C	17:34-18:19	>0.34
10-30-76	34M	03:17-03:33	B	0.13±0.02	29C	03:14-04:32	0.18±0.03
	35M	05:22-06:22	F	0.15±0.02	30C	05:17-06:26	0.11±0.02

* F = in freeway
B = background site

Differences between various combinations of numbers in Tables 2 and 3 are given in Tables 4 and 5. The right and left hand columns contain differences between freeway and background measurements which relate to the excess concentration of sulfur containing aerosol found on the roadway. The middle columns in Tables 4 and 5 contain differences between the data from the two LPI's when the vehicles transporting them were side-by-side at the background site. These data show that there is a sampling bias, which is discussed further in Section 3.5.

Tables 6 and 7 contain summaries of the meteorological data collected at the Caltech van and also data obtained later from the Southern California Air Pollution Control District.

Traffic data were also obtained from the California Department of Transportation (Caltrans), when they were available, for the portions of the freeway under study. Data for the Santa Monica Freeway on 21 October have been extracted and tabulated, and are given in Table 8. No traffic data are available for the Ventura Freeway on 26 October, which is the other day of in-roadway measurements in normal traffic selected for intensive analysis in this Report. In Table 8, the traffic volumes tabulated are the hourly totals for the hour ending after the time of the run. Traffic count data are available every few miles along the Santa Monica Freeway, and the data from the traffic sensor nearest the location of the van during each run were used.

2.3 THE UNIVERSITY OF MINNESOTA DATA

The University of Minnesota participants in this study were associated with Professor K. T. Whitby, and a key role in the field operations and data analysis was played by Bruce Cantrell. The main activity of the University of Minnesota was to operate a mobile laboratory alternately on the freeway and at the background sites. Figures 2 and 3 show the layout of the instrumentation in the van and the location of the air sample inlet tubes. For most of the experiments air samples were collected through the tubes which have an inlet just above the headlights on the van. Figure 4 shows the calculated transport efficiency as a function of particle size of the sampling tubes.

Table 9 gives a listing of the equipment in the van, and the mnemonics used to refer to the equipment or the experimental data derived from the equipment. Because the aerosol measuring equipment requires several minutes to determine a size spectrum, bag samples were collected about every four minutes, and then the size distribution of the aerosol in the bag was determined. Data from the trace gas measuring instruments were recorded every half second, then averaged over the time of each bag fill.

Table 4. Total Sulfur Differences Calculated from Low Pressure Impactor Data

Date	Daily Average Freeway - Background from LPI in U. Minn. Van μg/m^{3}S	Difference at Background Site LPI in U. Minn. Van - LPI in Caltech Van μg/m^{3}S	Difference Between LPI U. Minn. Van Freeway - LPI Caltech Van Background μg/m^{3}S
19 October	0.37	-2.12	-2.79
20 October	0.92	-1.08	-0.91 -1.83
21 October	-0.10	0.04	-0.56 0.01
22 October	0.13	-0.38	-0.59 -0.19
24 October	-0.83	-0.63	-0.57 -0.61
25 October	0.39	-0.74	-0.98 -0.26
26 October	-0.15	-0.07	-0.11 0.06
27 October AM	0.19	-0.07	-0.06 -0.17
27 October PM	0.23	-0.27	-0.30 -0.41
28 October	0.45	-0.12	-0.30
30 October	-0.13	-0.30	-0.54
Mean	0.13	-0.52	-0.58
Std. Deviation	0.45	0.63	0.69

Table 5. Sulfur Differences in Particles Smaller than 0.12 µm Calculated from Low Pressure Impactor Data

Date	Daily Average Freeway - Background from LPI in U. Minn. Van µg/m^{3}S x 10^2	Difference at Background Site LPI in U. Minn. Van - LPI in Caltech Van µg/m^{3}S x 10^2	Difference Between LPI U. Minn. Van Freeway - LPI Caltech Van Background µg/m^{3}S x 10^2
19 October	2	-7	-1
20 October	5.8	7	12 -8
21 October	12.5	-3	1 15
22 October	12.5	-5	23 10
24 October	6	-4	-5 17
25 October	13	-2	6 12
26 October	4	0	2 9
27 October AM	11.5	7	10 -2
27 October PM	4	7	-8 2
28 October	61	-1	
30 October	2	-5	4
Mean	12.2 7.3	-0.5	5.5
Std. Deviation	16.7 4.5	5.2	8.7
	All Data Without 28 October		

Table 6. Weather Summary from Caltech Van Data

Date	Time	Wind Speed	Wind Direction	
10/20/76	15:00-19:00	1-2 mph	WSW	Cloudy
10/21/76	8:00-10:00	~ 0	below threshold	Cloudy
	10:00-11:00	~ 1 mph	SSW	
10/22/76	7:00- 8:45	~ 0	below threshold	Overcast
	8:45-11:00	1-2 mph	SW	
10/24/76	15:15-17:30	2 mph	SW	Sunny
10/25/76	16:00-18:00	5 mph	W	
	18:00-19:30	~ 1 mph	NW (?)	
10/26/76	14:30-18:00	5-10 mph	ENE	Clear & Sunny Santa Ana Winds
10/27/76	7:00-9:30	~ 0	below threshold	
	9:30-10:30	~ 1 mph	W	
	15:00-17:30	5 mph	NE	Clear,Santa Ana Winds
10/28/76	15:00-17:00	2 mph	S	Sunny
	17:00-18:00	0	below threshold	
10/30/76	3:15- 6:30	0	below threshold	no fog

10/19/76 No Data

Table 7. Weather Summary from Air Pollution Control District Data

Date	Wind Station	Time (PDT)	Wind Speed (mph)	Wind Direction
10/19/76	Downtown (75W)	14:00-18:00	7	SW
	Compton (112W)		12	SW
	West L.A. (102W)		4	WSW
10/20/76	Downtown	15:00-19:00	5	SW
	Compton		9	SSW
	West L.A.	" "	3	SW
10/21/76	Downtown	8:00-11:00	3	W
	West L.A.	8:00-11:00	3	WSW
10/22/76	Downtown	7:00-9:00 9:00-11:00	5 5	SW/SW SW
	Compton	7:00-9:00 9:00-11:00	2 7	SW SW
	West L.A.	7:00-9:00 9:00-11:00	2 3	WNW SW
10/24/76	Downtown	15:00-18:00	6	SW
	West L.A.	" "	4	SW
	Compton	" "	10	WSW
10/25/76	West L.A.	16:00-18:00 18:00-20:00	5 3	SW W
10/26/76	Reseda(107W)	14:00-18:00	13	ENE
10/27/76	Pico Rivera (134W)	7:00-11:00	4	N
	Reseda	15:00-18:00	7	NNE
10/28/76	West L.A.	15:00-17:00 17:00-19:00	4 1	SW SE

Table 8. Traffic Data for the Santa Monica Freeway on 21 October 1977

U. Minn. Run No. *	Traffic Volume vehicles/hour East Bound	West Bound	Total
5	5320	4659	9979
6	5035	4603	9638
7	6160	4025	10185
8	6160	4025	10185
9	5320	4659	9979
10	5320	4659	9979
11	6160	4025	10185
12	6160	4025	10185
13	5320	4659	9979
14	5674	4438	10112
15	5744	4016	9760
16	5674	4438	10112
17	5960	4752	10712
18	6140	4161	10301
19	5960	4752	10712

*See Tables 14 and 21 for times and locations

VEHICLE LEFT SIDE

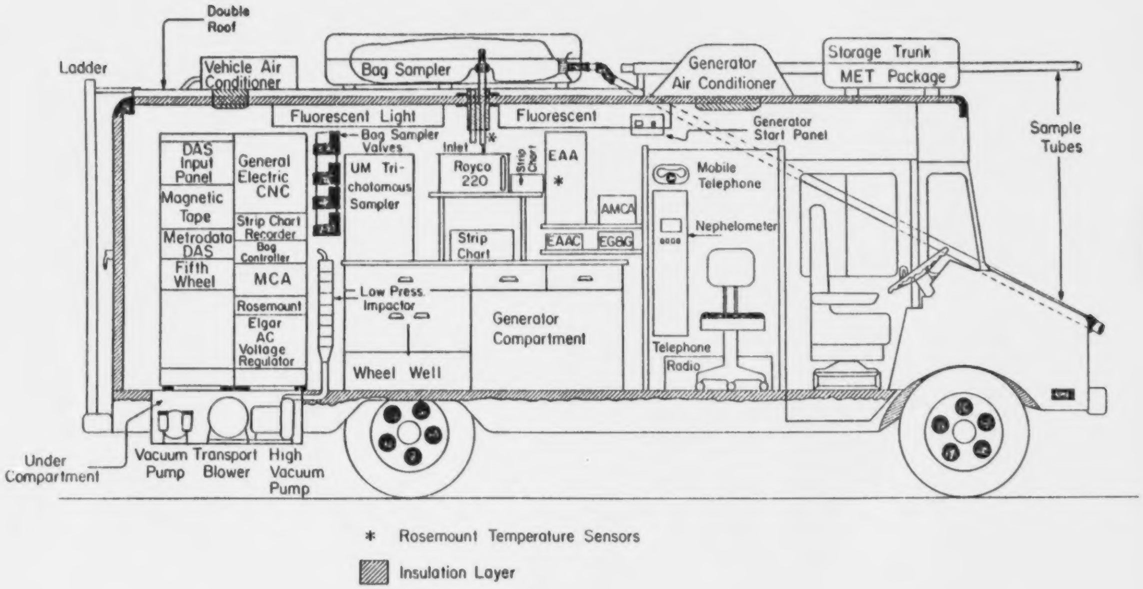

Double Roof
Ladder
Vehicle Air Conditioner
Bag Sampler
Generator Air Conditioner
Storage Trunk
MET Package
Fluorescent Light
Fluorescent
Generator Start Panel
Sample Tubes
Bag Sampler Valves
Inlet
DAS Input Panel
General Electric CNC
Magnetic Tape
Metrodata DAS
Strip Chart Recorder
Bag Controller
Fifth Wheel
MCA
Rosemount
Elgar AC Voltage Regulator
UM Tri-chotomous Sampler
Royco 220
Strip Chart
EAA
*
AMCA
EAAC
EG&G
Strip Chart
Mobile Telephone
Nephelometer
Low Press. Impactor
Wheel Well
Generator Compartment
Telephone
Radio
Under Compartment
Vacuum Pump
Transport Blower
High Vacuum Pump
* Rosemount Temperature Sensors
Insulation Layer

Figure 2. Layout of the Left Side of the University of Minnesota Van

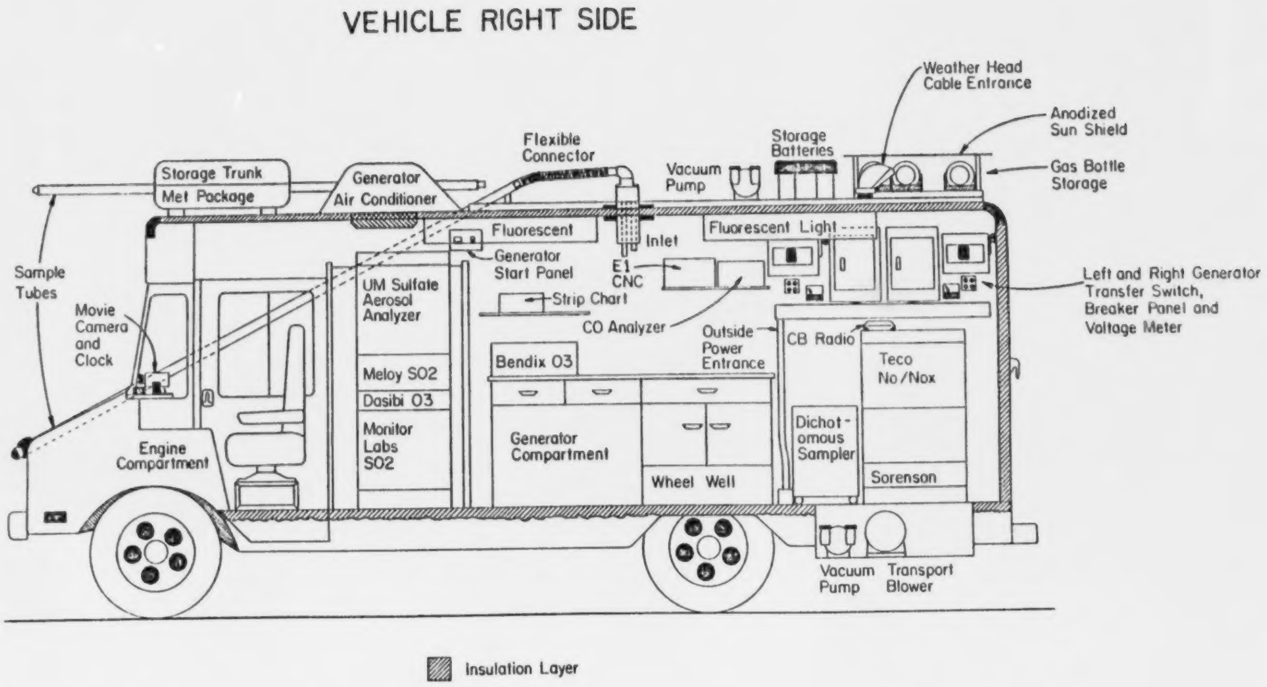

VEHICLE RIGHT SIDE
Sample Tubes
Movie Camera and Clock
Storage Trunk
Met Package
Engine Compartment
Generator Air Conditioner
Flexible Connector
Fluorescent
Generator Start Panel
Strip Chart
UM Sulfate Aerosol Analyzer
Meloy SO2
Dasibi O3
Monitor Labs SO2
Bendix O3
Generator Compartment
Inlet
E1 CNC
CO Analyzer
Vacuum Pump
Storage Batteries
Fluorescent Light
Wheel Well
Outside Power Entrance
CB Radio
Teco No/Nox
Dichotomous Sampler
Sorenson
Vacuum Pump
Transport Blower
Weather Head Cable Entrance
Anodized Sun Shield
Gas Bottle Storage
Left and Right Generator Transfer Switch, Breaker Panel and Voltage Meter
▨ Insulation Layer

Figure 3. Layout of the Right Side of the University of Minnesota Van

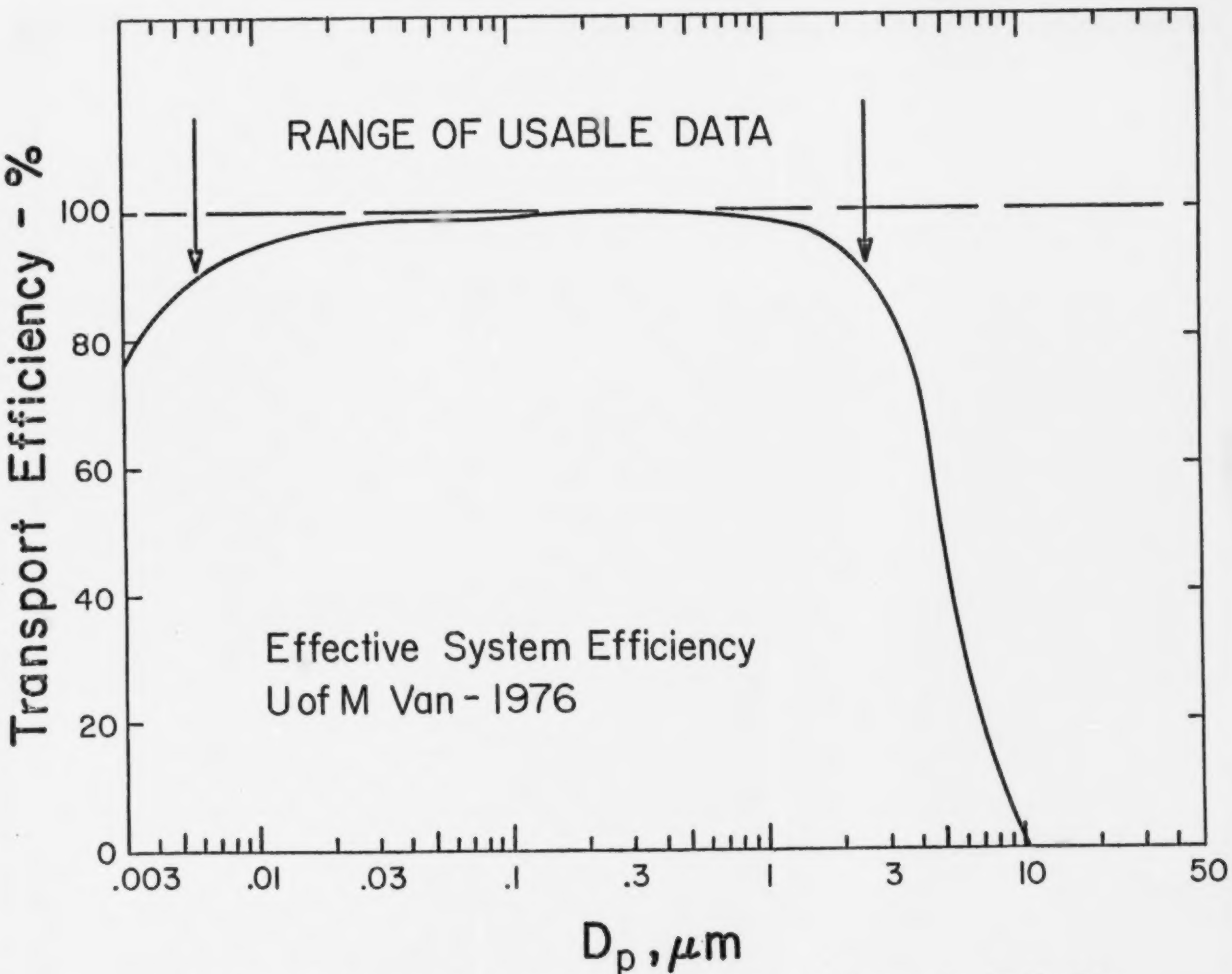


Figure 4. Calculated Transport Efficiency of the University of Minnesota Van Sampling Tubes

Table 9. Nomenclature, a Description of Terms and Units

Below are listed the mnemonics, definitions and units for the various parameters referred to in the text.

General

TIME	Hours, Pacific Standard Time
DATE	Julian date; expressed, 294J/1976
SITE	Designator for freeway, 8 ASCII characters
PASS LABEL	Designator for pass on freeway

Meteorology

WDIR, WD	Wind direction, clockwise degrees from north
WSPD, WSP	Wind speed, kilometers/hr.
TOUT	Outside temperature, °C
TIN	Inside temperature, °C
TEAA	EAA classifier temperature, °C
DEWPT, TDP	Dew point, °C
RH, RELHUM	Relative humidity, percent

Gas Chemistry

SO2	Sulfur gas, PPM
O3	Ozone, PPM
CO	Carbon monoxide, PPM
NO	Nitric oxide, PPM
NO2	Nitrogen dioxide, PPM
NOX	Total oxides of nitrogen, PPM

Equipment References

EAA	Electrical aerosol analyzer; Thermo-Systems, Model 3030
CNC	Condensation nuclei counter; Environment One, Model RICH 100
ROYCO 220, R220	Optical particle counter; Royco, Model 220
SO2	Sulfur analyzer; Monitor Labs, Model 8450
O3	Ozone monitor; Dasibi Environmental Corp., Model 1003-AH
CO	Carbon monoxide monitor; Energetics Science, Inc.
NO, NOX	Chemiluminescent NO-NO_2-NO_x analyzer; Thermo Electron Corp., Series 14
LBL	Dichotomous filter sampler; Lawrence Berkeley Labs.
TCS	Trichotomous filter sampler; Particle Technology Laboratory, University of Minnesota
LPI	Low pressure impactor; Keck Labs., California Institute of Technology

Particle Size Distribution

DP	Particle diameter-interval boundary, μm
DPI	Particle diameter-geometric midpoint of size interval, μm
DN	Particle number concentration, in a size interval, no./cc
DN/DLDP	Particle number concentration per log-size interval, no./cc log D_p
DS	Surface area concentration, in a size interval, μm^2/cc
DS/DLDP	Surface area concentration per log-size interval, μm^2/cc log D_p
DV	Volume concentration, in a size interval, μm^3/cc
DV/DLDP	Volume concentration per log-size interval, μm^3/cc log D_p

Table 9. Nomenclature, a Description of Terms and Units (Continued)

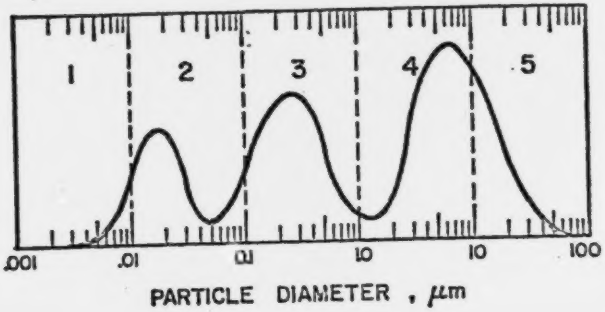


Illustration of Particle Size Subranges.

Integral Particle Parameters

BSCAT	Light scattering coefficient, m^{-1} (nephelometer data)
ANC, CNC	Aitken nuclei concentration, no./cc
1,2,3,4,5	Particle size subranges; see diagram above
NT,ST,VT	Total number, surface area, and volume concentrations
N2,S2,V2	Number, surface area, and volume concentrations in subrange-2
N3,S3,V3	Number, surface area, and volume concentrations in subrange-3
N4,S4,V4	Number, surface area, and volume concentrations in subrange-4
N5,S5,V5	Number, surface area, and volume concentrations in subrange-5
N3-,S3-,V3-	Number, surface area, and volume concentrations in subranges 2 & 3
N4+,S4+,V4+	Number, surface area, and volume concentrations in subranges 4 & 5

Accumulation Mode Parameters

NAC,SAC,VAC	Integral number, surface, and volume for the accumulation mode; respectively, no./cc, μm^2/cc, and μm^3/cc
DGN,DGS,DGV	Geometric mean size of accumulation mode in μm by weighting; respectively, number, surface, and volume
SGN,SGS,SGV	Geometric standard deviation of the accumulation mode in each of its weightings; respectively, number, surface, and volume
ANT	Total submicron aerosol number concentration obtained from the EAA; no./cc
ENV=(V3-)-(VAC)	Estimated nuclei mode volume; μm^3/cc

The aerosol and gas data resulting from one bag fill are reported in the following tabulations as a run, and appear in one line of the tables.

The calibration constants used in the reduction of the electrical aerosol analyzer (EAA) data are given in Table 10. They are the same as were used in the reduction of the data from the General Motors Sulfate Dispersion Experiment (Stevens, et al., 1976; Wilson et al., 1977). The calibration constants for the gas analyzers are given in Table 11.

A trichotomous sampler designed and built at the University of Minnesota was used in the field for the first time in this program. Its purpose is to collect size fractionated aerosol samples, and to include in the fractionation a cut between the nuclei and accumulation mode size range. A flow diagram of the instrument is given in Figure 5. A dichotomous sampler splits the aerosol into a flow containing the large particles (as well as some smaller particles) which passes through filter A, and a flow containing the particles smaller than 3.5 um which passes through filter B. A portion of the flow to filter B is drawn into an EAA, where it is further classified as shown in Figure 6. In the drift tube the nuclei mode particles migrate toward the central collector rod and are collected on filter D, and the larger particles, which have a smaller mobility, remain in the outer portion of the flow and are collected on filter C.

Another new instrument evaluated in the field was the electrostatically pulsed flame photometric detector, which is capable of separately determining the gas phase and the aerosol sulfur content of the atmosphere. A paper describing this instrument and its use in this program has been published by (Kittelson, McKenzie, Vermeersch, Dorman, Pui, Linne, Liu, and Whitby, 1978). Figures 11 and 12 of this article show data obtained in this program. It was not practical to obtain in-roadway data with the version of the instrument in use in October, 1976, because the fluctuations of the in-roadway sulfur gas concentration contained a large signal component at the same frequency as was used for the electrostatic chopping, and this caused interferences between the gas phase and the aerosol sulfur output signals. The instrument performed well when data were recorded away from the concentration fluctuations typical of the environment near roadways.

The schedule of all the daily experiments is given in Table 12. More detailed schedules for the days selected for analysis are given in Tables 13 to 19. Figure 7 gives the configuration of the vehicles on 30 October, when several catalyst equipped cars were driven ahead of the Washington University car and the University of Minnesota van. Summaries or data maps of the results obtained on days for which the data have been processed are given in Tables 20 through 26. Daily averages from these

Table 10

Electrical Aerosol Analyzer Constants for nt = 10^7 $cm^{-3}sec^{-1}$

$$\Delta N_i = (\Delta N/\Delta I)_i \Delta I_i = (\Delta N/\Delta I_i)_i \ (I_{i+1} - I_i)$$

		$(\Delta N/\Delta I_i)$ particle/pa	
Channel No.	Dpi - μm	(B) Liu - Pui	(HC) Whitby - Cantrell
1	.0042	——	——
2	.0075	9.52×10^6	1.36×10^6
3	.0133	4.17×10^5	3.16×10^5
4	.0237	1.67×10^5	1.53×10^5
5	.0422	8.70×10^4	1.57×10^5
6	.075	4.44×10^4	3.09×10^4
7	.133	2.41×10^4	2.43×10^4
8	.237	1.23×10^4	1.52×10^4
9	.422	6.67×10^4	5.68×10^3
10	.750	3.51×10^3	1.33×10^3

Note: Constants HC developed for DPGVAN = .04 μm,
SGN = 1.7, VAN = 1 $\mu m^3 cm^{-3}$, DPGVAC = 0.35 μm,
SGAC = 2 and VAC = 30 $\mu m^3 cm^{-3}$

Table 11. Gas Calibration Constants[*]

		SO_2		O_3		NO		NO_x	
Date	Julian Date	B[†] ppm/volt	A[†] ppm	B ppm/volt	A ppm	B ppm/volt	A ppm	B ppm/volt	A ppm
19 Oct 76	293	10.002	0.00006	0.972	-0.0058	0.0885	0.0136	0.0891	0.0138
20 Oct 76	294	10.002	-0.00054	0.896	0.0	0.0968	0.0043	0.0962	0.0030
21 Oct 76	295	10.076	-0.00380	0.879	0.0	0.1818[ϕ]	0.0172	0.1832[ϕ]	0.0154
22 Oct 76	296	9.945	-0.00157	1.210	0.0	0.2040	-0.0108	0.2043	-0.0137
24 Oct 76	298	10.104	-0.00097	1.114	0.0	0.2024	0.0163	0.2041	0.0142
25 Oct 76	299	10.049	-0.00056	1.139	0.0	0.2103	0.0005	0.2117	0.0008
26 Oct 76	300	10.020	0.00119	1.286	0.0	0.2105	0.0104	0.2126	0.0070
27 Oct 76	301[#]	9.979	0.00085	1.265	-0.00125	0.2114	0.0061	0.2136	0.0004
28 Oct 76	302	9.937	0.00051	1.243	-0.0025	0.2122	0.0018	0.2146	-0.0062
29 Oct 76	303	9.944	0.00199	1.195	-0.0024	0.2090	0.0140	0.2091	0.0140

* These are reduction constants used to obtain the listed data. Instruments were calibrated on the following ranges: SO_2 - 1 ppm; O_3 - 1 ppm; NO-NO_x - 1 ppm.

ϕ The NO-NO_x was changed to 2 ppm full scale.

† B is the slope and A is the intercept for the algorithm: CONCENTRATION (PPM) = A + (OUTPUT VOLTAGE)B

Constants for 301 are interpolations of those for 300 and 302.

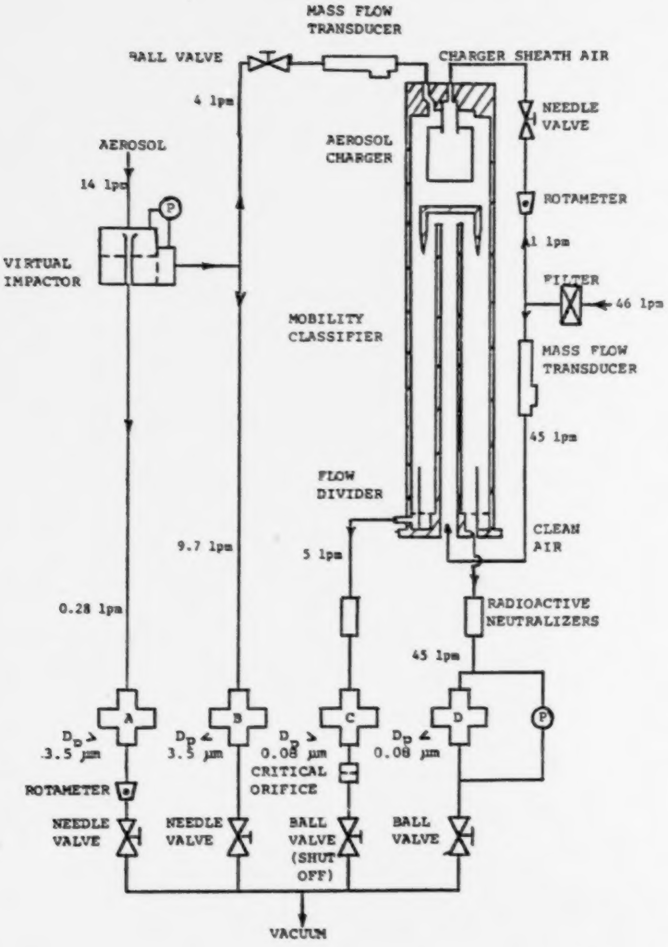

MASS FLOW TRANSDUCER
BALL VALVE
CHARGER SHEATH AIR
4 lpm
NEEDLE VALVE
AEROSOL
AEROSOL CHARGER
14 lpm
P
ROTAMETER
1 lpm
VIRTUAL IMPACTOR
FILTER
46 lpm
MOBILITY CLASSIFIER
MASS FLOW TRANSDUCER
45 lpm
FLOW DIVIDER
9.7 lpm
5 lpm
CLEAN AIR
0.28 lpm
RADIOACTIVE NEUTRALIZERS
45 lpm
A
B
C
D
P
$D_p >$ 3.5 μm
$D_p <$ 3.5 μm
$D_p >$ 0.08 μm
$D_p <$ 0.08 μm
CRITICAL ORIFICE
ROTAMETER
NEEDLE VALVE
NEEDLE VALVE
BALL VALVE (SHUT OFF)
BALL VALVE
VACUUM

Figure 5. Flow Diagram of the Trichotomous Sampler

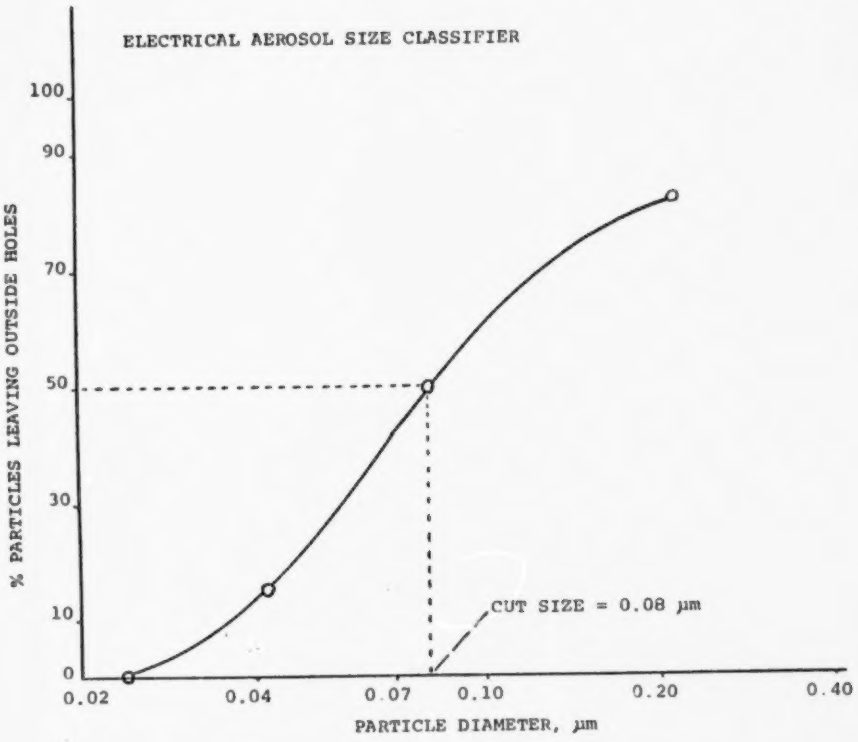


Figure 6. Classification Efficiency of the Trichotomous Sampler. The Outside Holes Lead to Filter D.

Table 12. EXPERIMENT SCHEDULE

Experiment No.	Rockwell No.	Date	Location of Run	NOTE: Period /Wind	Apparent /Aerosol Loading
1	293	19-OCT-76	Harbor	Afternoon/light cross	/moderate bkgnd.
2*	294	20-OCT-76	Santa Monica	Afternoon/parallel light	/moderate bkgnd.
3*	295	21-OCT-76	Santa Monica	Morning /near stag.	/moderate bkgnd.
4	296	22-OCT-76	Harbor	Morning /near stag.	/light bkgnd.
5	298	24-OCT-76	Santa Monica/ Harbor	Afternoon/light	/light bkgnd.
6	299	25-OCT-76	San Diego	Afternoon/light cross	/moderate bkgnd.
7*	300	26-OCT-76	Ventura	Afternoon/Santa Ana cross	/very light bkgnd.
8*	301A	27-OCT-76	San Bernardino	Morning /parallel near stag.	/moderate bkgnd.
9*	301B	27-OCT-76	Ventura	Afternoon/Santa Ana cross	/very light bkgnd.
10*	302	28-OCT-76	San Diego	Afternoon/light cross	/very light bkgnd.
11	303	29-OCT-76	San Diego	Afternoon/light cross	/light bkgnd.
12*	304	30-OCT-76	I-210	Early morn./stag.	/moderate bkgnd.

*Selected for analysis

Table 13.

Experiment 2/294, Santa Monica Freeway, 20 October 1976

Pass #	Time		End Points		Time		Filter Location	Pass Label
	Start	Stop	Start	End	Start	Stop		
1	14:50:00 to	15:36:00	Background at Exposition Park		14:50:00 to	15:31:00	Exposition Park	Background
2	15:43:25 to	15:53:50	Vermont Ave. to	National Blvd.	15:44:20	-		A to B
3	15:55:10 to	16:03:15	National Blvd. to	Vermont Ave.	-	-	-	B to A
4	16:06:40 to	16:15:00	Vermont Ave. to	National Blvd.	-	16:14:20	-	A to B
5	16:17:00 to	16:24:15	National Blvd. to	Vermont Ave.	-	-	-	B to A
6	16:35:00 to	17:15:57	Background at Exposition Park		16:35:00 to	17:05:00	Exposition Park	Background
7	17:40:30 to	17:51:43	Vermont Ave. to	National Blvd.	17:40:30	-	Vermont Ave.	A to B
8	17:54:20 to	18:02:00	National Blvd. to	Vermont Ave.	-	-	-	B to A
9	18:05:30 to	18:18:00	Vermont Ave. to	National Blvd.	-	18:15:30	-	A to B
10	18:20:00 to	18:27:30	National Blvd. to	Vermont Ave.	-	-	-	B to A
11	18:52:00 to	19:25:12	Background at Exposition Park		18:52:00 to	19:22:00	Exposition Park	Background

Table 14.

Experiment 3/295, Santa Monica Freeway, 21 October 1976

	Time		End Points		Time			
Pass #	Start	Stop	Start	End	Start	Stop	Filter Location	Pass Label
1	07:05:30 to	07:32:00	Background at Rancho Park		07:12:00 to	07:32:00	Rancho Park	Background
2	08:00:00 to	08:13:50	Overland Ave. to	Vermont Ave.	08:00:00	-	Overland Ave.	A to B
3	08:15:20 to	08:23:40	Vermont Ave. to	National Blvd.	-	-	-	B to C
4	08:27:00 to	08:38:00	National Blvd. to	Vermont Ave.	-	08:38:00	Vermont Ave.	C to B
5	08:41:00 to	08:49:25	Vermont Ave to	Overland Ave.	-	-	-	B to A
6	09:45:00 to	09:53:40	Overland Ave. to	Vermont Ave.	09:45:05	-	Overland Ave.	A to B
7	09:55:20 to	10:03:00	Vermont Ave. to	National Blvd.	-	-	-	B to C
8	10:04:30 to	10:12:30	National Blvd. to	Vermont Ave.	-	-	-	C to B
9	10:14:40 to	10:23:30	Vermont Ave. to	Overland Ave.	-	10:23:30	Overland Ave.	B to A
10	10:45:00 to	11:15:00	Background at Rancho Park		10:45:00 to	11:15:00	Rancho Park	Background

Table 15.

Experiment 7/300, Ventura Freeway, 26 October 1976

Pass #	Time		End Points		Time		Filter Location	Pass Label
	Start	Stop	Start	End	Start	Stop		
1	13:31:25 to	13:51:30	Hill Ave. to Hayvenhurst Ave.		13:36:00	-	134 and I5	A to B
2	13:53:00 to	13:56:10	Hayvenhurst Ave. to Van Nuys Blvd.		-	13:56:10	Van Nuys Blvd.	B to C
3	14:07:24 to	15:04:35	Background at Sherman Oaks Park		14:11:00 to	14:56:00	Sherman Oaks Park	Background
4	15:09:10 to	15:20:30	Van Nuys Blvd. to Topanga Canyon Blvd.		15:09:10	-	Van Nuys Blvd.	C to D
5	15:23:15 to	15:48:20	Ventura Blvd. to Central Ave.		-	-	-	E to F
6	15:51:00 to	16:09:31	Central Ave. to Van Nuys Blvd.		-	16:09:31	Van Nuys Blvd.	F to C
7	16:17:20 to	17:20:00	Background at Sherman Oaks Park		16:23:00 to	17:08:02	Sherman Oaks Park	Background
8	17:25:05 to	17:41:00	Van Nuys Blvd. to Topanga Canyon Blvd.		17:25:05	-	Van Nuys Blvd.	C to D
9	17:42:00 to	18:26:30	Topanga Canyon Blvd. to Hill Ave.		-	18:26:30	Hill Ave.	D to A

Table 16.

Experiment 8/301A, San Bernardino, 27 October 1976

	Time		End Points		Time			
Pass #	Start	Stop	Start	End	Start	Stop	Filter Location	Pass Label
1	06:52:15 to	07:00:50	Rosemead Blvd. to	Atlantic Blvd.	06:52:30	-	Rosemead Blvd.	A to B
2	07:02:30 to	07:17:50	Atlantic Blvd. to	Azusa Ave.	-	-	-	B to C
3	07:19:50 to	07:43:30	Azusa Ave. to	Atlantic Blvd.	-	-	-	C to B
4	07:45:20 to	07:49:30	Atlantic Blvd. to	Rosemead Blvd.	-	07:49:30	Rosemead Blvd.	B to A
5	07:59:20 to	08:22:00	Background 1 at	Rosemead Blvd.	-	-	-	Background1
6	08:27:50 to	08:32:45	Rosemead Blvd. to	Atlantic Blvd.	08:28:00	-	Rosemead Blvd.	A to B
7	08:34:40 to	08:50:45	Atlantic Blvd. to	Azusa Ave.	-	-	-	B to C
8	08:52:00 to	09:07:45	Azusa Ave. to	Garfield Ave.	-	-	-	C to D
9	09:09:25 to	09:21:35	Garfield Ave. to	Pacific Ave.	-	09:21:35	Pacific Ave.	D to E
10	09:45:30 to	10:58:00	Background 2 at	Del Norte Park	09:45:30 to	10:33:30	Del Norte Park	Background2

Table 17.
Experiment 9/301B, Ventura Freeway, 27 October 1976

Pass #	Time		End Points		Time		Filter Location	Pass Label
	Start	Stop	Start	End	Start	Stop		
1	13:43:34 to	14:18:10	Hill Ave. to	Topanga Cyn. Blvd	13:55:30	-	Riverside Dr.	A to B
2	14:19:40 to	14:44:20	Topanga Cyn. Blvd. to	Central Ave.	-	-	-	B to C
3	14:47:40 to	15:00:40	Central Ave. to	Van Nuys Blvd.	-	15:00:41	Van Nuys Blvd.	C to D
4	15:15:40 to	16:28:32	Background at Sherman Oaks Park		15:15:40 to	16:15:30	Sherman Oaks Park	Background
5	16:40:30 to	17:01:30	Van Nuys Blvd. to	Malibu Canyon Road	16:40:30	-	Van Nuys Blvd.	D to E
6*	17:03:00 to	17:35:45	Malibu Canyon Road to	Laurel Canyon Blvd.	-	17:35:45	Laurel Canyon Blvd.	E to F
7⁺	18:10:00 to	18:12:24	Pass Ave. to	Forest Lawn Dr.	18:10:00 to	18:10:20	Pass Ave.	G to H
8	18:15:50 to	18:17:06	Forest Lawn Dr. to	Victory Blvd.	-	-	-	H to I

* Trailer generator muffler problem; stopped at Pass Ave. for repair.

⁺ Electrical problem in LBL; turned off at Forest Lawn Drive.

Table 18.
Experiment 10/302, LACS, 28 October 1976

	Time		End Points		Time			
Pass #	Start	Stop	Start	End	Start	Stop	Filter Location	Pass Label
1	15:57:29 to	17:12:40	Background at LACS Site		16:16:00 to	17:17:03	LACS	Background
2	17:40:40 to	17:53:40	Wilshire Blvd. to	LaTijera Blvd.	17:40:40	-	Wilshire Blvd.	A to B
3	17:55:30 to	18:33:30	LaTijera Blvd. to	Mulholland Dr.	-	-	-	B to C
4	18:36:00 to	18:42:17	Mulholland Dr. to	Wilshire Blvd.	-	18:42:17	Wilshire Blvd.	C to A
5*	18:54:00 to	19:03:36	LACS Site		-	-	-	LACS

* Wind had shifted; now blowing from the Freeway.

Table 19.
Experiment 12/304, Foothill, 30 October 1976

Pass #	Time		End Points		Time		Filter Location	Pass Label
	Start	Stop	Start	End	Start	Stop		
1*	3:17:05 to	3:33:45	Lake Ave. to	Ocean View Blvd.	+(3:17:05) to	+(3:33:45)	A to B	A to B
2	3:38:30 to	3:41:30	Ocean View Blvd. to	Lowell Ave.	3:38:30	-	Ocean View Blvd.	B to C
3	3:42:30 to	4:07:45	Lowell Ave. to	Irwindale Ave.	-	-	-	C to D
4	4:09:00 to	4:36:20	Irwindale Ave. to	Lowell Ave.	-	-	-	D to C
5	4:37:20 to	4:48:30	Lowell Ave. to	Lake Ave.	-	4:48:30	Lake Ave.	C to A
6	5:22:20 to	5:36:45	Lake Ave. to	Lowell Ave.	5:25:23	-	Lake Ave.	A to C
7	5:38:10 to	6:06:40	Lowell Ave. to	Irwindale Ave.	-	-	-	C to D
8	6:07:40 to	6:22:30	Irwindale Ave. to	Lake Ave.	-	6:22:30	Lake Ave.	D to A

*Off to repair LBL
+TCS times

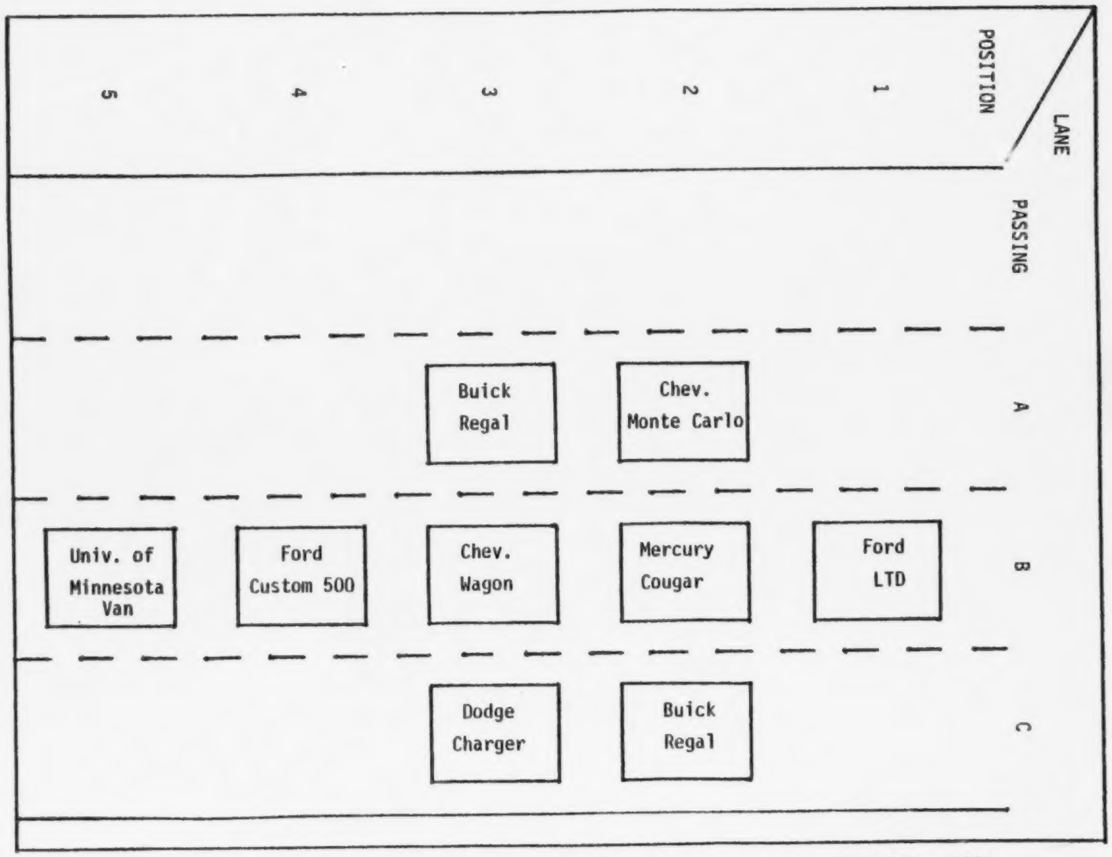

LANE
POSITION
PASSING
A
B
C
1
2
3
4
5
Ford LTD
Chev. Monte Carlo
Mercury Cougar
Buick Regal
Buick Regal
Chev. Wagon
Dodge Charger
Ford Custom 500
Univ. of Minnesota Van

Figure 7. VEHICLE POSITIONS - Experiment 12/306, Foothill, 30 October 1976

Table 20. Experiment No. 2, 20 October 1976 Afternoon

DATA MAP: VAN SAN MON 294J /76 PROCESS DATE: 14-JAN-77

RUN#	TIME	RH%	TOUT	DEWPT	SO2	O3	NO	NOX	CO	CNC	ANT	V3-	ENV	VAC	DPO VAC	SO VAC	PASS LABEL
1	14:50:08	62.	25.1	17.2	0.030	0.057	0.019	0.125	4.6	2.2E+05	1.3E+05	20.33	-1.06	21.38	0.22	1.85	B'KGND
2	14:56:43	58.	24.7	15.7	0.033	0.060	0.012	0.121	4.2	2.5E+05	1.3E+05	18.87	-1.34	20.21	0.23	1.87	B'KGND
3	15:03:17	58.	25.1	16.3	0.029	0.061	0.014	0.126	4.8	5.3E+05	1.9E+05	20.50	-1.49	21.98	0.23	1.90	B'KGND
4	15:09:51	56.	25.4	16.1	0.029	0.064	0.011	0.112	3.7	2.2E+05	1.2E+05	18.80	-1.35	20.15	0.23	1.86	B'KGND
5	15:16:24	60.	25.2	16.9	0.027	0.062	0.011	0.111	3.6	3.0E+05	3.1E+05	19.92	-1.20	21.13	0.24	1.88	B'KGND
6	15:22:58	62.	24.9	17.1	0.024	0.053	0.011	0.115	4.0	2.7E+05	1.7E+05	26.33	-1.32	27.65	0.23	1.81	B'KGND
7	15:29:31	61.	24.9	16.9	0.022	0.055	0.010	0.120	4.8	2.9E+05	1.1E+05	17.49	-1.14	18.63	0.23	1.88	B'KGND
8	15:49:12	62.	26.7	18.8	0.045	0.002	0.797	0.956	21.9	5.0E+06	2.2E+06	34.02	5.24	28.78	0.17	2.13	A TO B
9	15:55:45	63.	24.6	17.0	0.022	0.018	0.380	0.489	13.6	2.9E+06	2.3E+06	32.70	4.43	28.27	0.19	2.19	B TO A
10	16:02:18	59.	26.2	17.6	0.036	0.005	1.104	1.280	26.7	6.1E+06	3.3E+06	80.72	-1.37	82.09	0.20	2.15	B TO A
11	16:08:51	62.	26.4	18.5	0.047	0.011	0.922	1.103	25.6	4.3E+06	2.4E+06	43.45	2.16	41.29	0.18	2.24	A TO B
12	16:20:19	64.	25.7	18.3	0.030	0.029	0.848	0.983	18.7	6.2E+06	2.6E+06	35.64	5.29	30.35	0.16	2.17	B TO A
13	16:35:03	78.	23.1	19.1	0.019	0.026	0.101	0.187	7.9	3.6E+05	1.3E+05	11.23	0.09	11.14	0.19	2.00	B'KGND
14	16:41:36	75.	23.1	18.5	0.016	0.036	0.032	0.107	3.9	2.8E+05	8.3E+04	8.52	-0.28	8.79	0.20	1.99	B'KGND
15	16:46:30	73.	23.3	18.2	0.016	0.034	0.026	0.105	3.9	2.8E+05	1.3E+05	7.56	0.33	7.23	0.18	1.84	B'KGND
16	16:53:03	77.	23.3	19.0	0.015	0.034	0.021	0.092	3.3	2.8E+05	1.0E+05	7.27	-0.04	7.31	0.20	1.90	B'KGND
17	16:57:57	75.	23.3	18.6	0.018	0.022	0.028	0.114	4.7	3.0E+05	1.7E+05	7.38	-0.19	7.57	0.20	2.02	B'KGND
18	17:11:02	79.	23.1	19.3	0.015	0.007	0.032	0.122	7.2	3.2E+05	1.3E+05	7.10	0.05	7.04	0.18	1.95	B'KGND
19	17:15:57	76.	23.1	18.6	0.013	0.015	0.030	0.114	4.2	2.6E+05	2.2E+05	10.55	-0.15	10.70	0.18	1.94	B'KGND
20	17:45:24	75.	24.1	19.3	0.032	0.002	0.625	0.723	20.8	4.1E+06	2.8E+06	27.95	6.07	21.88	0.12	2.12	A TO B
21	17:58:30	72.	23.5	18.0	0.030	0.009	0.586	0.664	19.5	4.6E+06	2.9E+06	31.45	6.55	24.90	0.12	2.05	B TO A
22	18:11:36	74.	23.6	18.6	0.032	0.002	0.788	0.891	23.3	4.5E+06	3.1E+06	32.31	5.10	27.21	0.12	2.22	A TO B
23	18:16:30	78.	23.6	19.6	0.032	0.002	0.890	1.009	22.9	5.4E+06	3.1E+06	23.45	6.98	16.47	0.13	2.11	A TO B
24	18:23:03	79.	22.9	19.1	0.030	0.014	0.779	0.862	22.1	5.3E+06	3.8E+06	34.23	6.91	27.32	0.14	2.33	B TO A
25	18:55:45	92.	21.0	19.8	0.014	0.002	0.040	0.098	4.2	2.4E+05	1.2E+05	4.82	0.00	4.81	0.16	2.09	B'KGND
26	19:00:40	80.	22.2	18.5	0.015	0.002	0.052	0.113	6.4	2.8E+05	1.3E+05	6.09	0.30	5.79	0.18	1.89	B'KGND
27	19:07:12	87.	20.9	18.5	0.012	0.003	0.035	0.090	2.8	2.5E+05	8.9E+04	4.84	-2.20	7.03	0.27	2.51	B'KGND
28	19:13:45	91.	20.9	19.4	0.015	0.002	0.025	0.080	2.9	2.3E+05	2.4E+05	7.15	0.73	6.43	0.16	2.02	B'KGND
29	19:18:39	85.	20.9	18.2	0.013	0.002	0.087	0.146	7.6	4.1E+05	1.5E+05	5.25	0.13	5.12	0.16	2.10	B'KGND
30	19:25:12	82.	20.9	17.7	0.017	0.003	0.031	0.085	2.4	2.5E+05	1.7E+05	4.82	0.47	4.35	0.15	1.91	B'KGND

NOTE: See Table 9 pages 18-19 for a description of column headings and units.

Table 21. Experiment No. 3, 21 October 1976 Morning

DATA MAP: VAN SAN MON 295J /76 PROCESS DATE: 14-JAN-77

RUN#	TIME	RH%	TOUT	DEWPT	SO2	O3	NO	NOX	CO	CNC	ANT	V3-	ENV	VAC	DPO VAC	SO VAC	PASS LABEL
1	7:11:47	80.	19.4	16.0	0.010	0.002	0.026	0.057	1.4	1.6E+05	1.1E+05	4.91	0.26	4.64	0.17	2.16	B'KGND
2	7:18:24	91.	20.2	18.8	0.010	0.002	0.034	0.069	1.5	1.5E+05	1.1E+05	2.01	0.25	1.76	0.10	1.59	B'KGND
3	7:24:59	90.	19.2	17.6	0.008	0.002	0.033	0.062	1.2	1.6E+05	1.0E+05	2.35	0.22	2.12	0.14	2.07	B'KGND
4	7:29:55	81.	20.2	16.9	0.008	0.002	0.047	0.079	1.6	1.7E+05	1.4E+05	2.83	0.04	2.78	0.15	2.14	B'KGND
5	8:00:04	81.	21.0	17.7	0.028	0.002	0.447	0.489	30.8	1.2E+06	8.9E+05	11.65	2.22	9.43	0.09	1.77	A TO B
6	8:06:39	84.	21.2	18.4	0.030	0.002	0.474	0.537	21.7	1.9E+06	2.1E+06	18.59	4.43	14.16	0.10	1.90	A TO B
7	8:11:35	78.	22.3	18.3	0.039	0.012	0.948	1.020	29.6	4.1E+06	3.1E+06	33.00	7.79	25.21	0.09	2.05	A TO B
8	8:18:09	75.	22.0	17.4	0.037	0.005	0.778	0.856	20.0	4.4E+06	2.5E+06	35.99	6.41	29.58	0.11	2.00	B TO C
9	8:23:05	75.	22.0	17.4	0.062	0.003	1.000	1.101	20.9	4.8E+06	4.2E+06	61.79	10.11	51.69	0.13	2.01	B TO C
10	8:29:38	80.	21.0	17.4	0.021	0.002	0.509	0.555	14.0	3.8E+06	1.8E+06	14.48	3.35	11.13	0.12	1.83	C TO B
11	8:34:34	76.	21.7	17.2	0.032	0.046	0.706	0.767	27.0	4.5E+06	2.7E+06	24.70	5.48	19.22	0.12	2.07	C TO B
12	8:41:07	76.	21.7	17.3	0.029	0.002	0.745	0.817	19.1	5.2E+06	2.9E+06	31.55	7.15	24.40	0.11	2.05	B TO A
13	8:46:03	73.	22.2	17.2	0.031	0.002	0.866	0.943	18.4	7.0E+06	4.0E+06	24.51	7.66	16.85	0.11	2.17	B TO A
14	9:45:03	81.	21.0	17.6	0.017	0.002	0.383	0.434	12.0	3.5E+06	2.9E+06	15.64	6.91	8.73	0.08	1.83	A TO B
15	9:51:38	75.	22.3	17.6	0.028	0.004	0.720	0.800	16.0	6.9E+06	4.6E+06	34.31	10.49	23.83	0.10	2.11	A TO B
16	9:58:13	71.	23.1	17.7	0.031	0.002	0.694	0.774	13.9	5.1E+06	2.6E+06	22.26	5.05	17.21	0.13	2.04	B TO C
17	10:04:47	77.	21.7	17.4	0.018	0.005	0.481	0.527	12.9	4.3E+06	3.8E+06	18.59	9.03	9.56	0.09	1.94	C TO B
18	10:11:20	72.	22.5	17.1	0.027	0.002	0.621	0.687	16.6	4.4E+06	2.8E+06	21.67	7.24	14.44	0.11	2.23	C TO B
19	10:17:54	71.	23.0	17.3	0.029	0.002	0.838	0.926	14.8	6.9E+06	3.8E+06	37.51	8.23	29.28	0.13	1.88	B TO A
20	10:45:21	79.	21.7	18.0	0.006	0.029	0.023	0.037	0.4	2.1E+05	5.6E+04	1.92	0.12	1.79	0.13	1.68	B'KGND
21	10:50:17	81.	22.0	18.6	0.006	0.030	0.021	0.039	0.5	2.1E+05	5.4E+04	2.01	0.11	1.91	0.15	1.59	B'KGND
22	10:56:50	81.	21.2	17.8	0.009	0.031	0.022	0.037	0.5	2.0E+05	4.5E+04	4.07	-0.78	4.85	0.27	2.01	B'KGND
23	11:03:24	82.	20.8	17.5	0.008	0.033	0.022	0.037	0.2	1.9E+05	3.8E+04	3.76	0.11	3.65	0.21	1.77	B'KGND
24	11:09:57	81.	20.6	17.1	0.008	0.038	0.022	0.033	-0.2	1.9E+05	3.4E+04	2.01	-0.06	2.07	0.18	1.90	B'KGND

NOTE: See Table 9 pages 18-19 for a description of column headings and units.

Table 22. Experiment No. 7, 26 October 1976 Afternoon

DATA MAP: VAN VENTURA 300J /76 PROCESS DATE: 14-JAN-77

RUN#	TIME	RH%	TOUT	DEWPT	SO2	O3	NO	NOX	CO	CNC	ANT	V3-	ENV	VAC	DPG VAC	SO VAC	PASS LABEL
1	13:31:25	0.	26.0	0.0	0.004	0.024	0.283	0.325	4.7	3.2E+06	1.1E+06	5.68	1.55	4.13	0.16	2.71	A TO B
2	13:34:11	0.	27.6	0.0	0.005	0.010	0.225	0.263	4.5	3.6E+06	2.2E+06	11.45	4.23	7.23	0.16	2.40	A TO B
3	13:47:47	0.	27.8	0.0	0.003	0.031	0.669	0.706	10.3	4.5E+06	2.0E+06	8.34	2.43	5.91	0.15	2.43	A TO B
4	13:54:20	0.	27.0	0.0	0.015	0.014	0.735	0.785	13.8	4.6E+06	1.8E+06	8.77	2.80	5.97	0.20	2.33	B TO C
5	14:07:24	0.	25.7	0.0	0.003	0.042	0.014	0.020	0.5	1.7E+05	5.0E+04	1.15	0.27	0.88	0.24	2.09	B'KGND
6	14:13:57	18.	25.2	-0.9	0.004	0.041	0.016	0.018	-0.1	1.7E+05	2.6E+04	0.99	-0.03	1.02	0.30	2.19	B'KGND
7	14:20:29	20.	25.7	1.0	0.002	0.045	0.019	0.025	0.0	1.7E+05	1.9E+04	0.89	0.24	0.66	0.22	1.90	B'KGND
8	14:27:01	20.	26.0	1.4	0.004	0.037	0.017	0.021	-0.2	1.7E+05	3.0E+04	1.09	-0.03	1.12	0.29	2.21	B'KGND
9	14:31:55	22.	25.6	2.1	0.002	0.044	0.016	0.022	-0.1	1.7E+05	2.5E+04	1.07	-0.19	1.26	0.34	2.19	B'KGND
10	14:38:27	23.	26.0	3.5	0.003	0.046	0.017	0.017	-0.3	4.9E+04	2.3E+04	1.18	0.23	0.96	0.26	1.79	B'KGND
11	14:44:59	22.	25.7	2.6	0.005	0.049	0.016	0.018	-0.5	4.1E+04	1.9E+04	0.98	0.23	0.75	0.22	1.78	B'KGND
12	14:51:31	21.	25.7	1.6	0.002	0.047	0.016	0.022	-0.4	6.5E+04	2.6E+04	0.81	0.09	0.72	0.24	2.06	B'KGND
13	14:58:03	21.	25.4	1.7	0.003	0.045	0.015	0.020	-0.4	5.5E+04	2.8E+04	0.96	0.23	0.73	0.23	1.80	B'KGND
14	15:04:35	23.	25.5	2.8	0.002	0.044	0.017	0.020	0.1	4.8E+04	3.2E+04	0.81	0.22	0.59	0.20	1.79	B'KGND
15	15:11:07	22.	27.0	3.3	0.003	0.003	0.271	0.301	6.8	0.0E-01	1.5E+06	7.61	2.61	5.00	0.13	2.39	C TO D
16	15:17:39	21.	26.5	2.6	0.007	0.012	0.544	0.582	8.2	0.0E-01	2.6E+06	11.85	5.25	6.60	0.12	2.27	C TO D
17	15:24:11	23.	25.7	3.3	0.003	0.012	0.729	0.770	10.0	0.0E-01	2.2E+06	7.62	2.75	4.86	0.14	2.39	E TO F
18	15:30:42	23.	27.0	3.9	0.013	0.012	0.909	0.956	14.3	0.0E-01	3.8E+06	15.67	7.19	8.48	0.17	2.17	E TO F
19	15:37:13	23.	26.8	4.2	0.012	0.018	0.667	0.705	16.5	0.0E-01	4.1E+06	41.35	6.13	35.22	0.18	2.19	E TO F
20	15:43:45	23.	26.8	3.9	0.012	0.003	0.449	0.484	9.5	0.0E-01	2.9E+06	14.69	5.59	9.10	0.16	2.22	E TO F
21	15:56:47	22.	27.6	3.7	0.023	0.017	1.139	1.179	15.2	0.0E-01	3.0E+06	18.99	5.03	13.97	0.19	2.32	F TO C
22	16:03:18	22.	26.8	3.5	0.001	0.028	0.372	0.391	21.7	1.1E+06	9.5E+05	18.37	0.12	18.26	0.16	2.35	F TO C
23	16:29:22	21.	25.9	2.0	0.002	0.028	0.019	0.032	1.6	8.4E+04	3.3E+04	1.41	0.44	0.98	0.25	1.86	B'KGND
24	16:35:53	20.	25.2	0.9	0.001	0.031	0.017	0.022	0.4	1.3E+05	3.6E+04	1.36	0.41	0.95	0.25	1.92	B'KGND
25	16:42:24	21.	25.5	1.4	0.004	0.037	0.016	0.022	-0.2	7.7E+04	3.7E+04	1.16	0.42	0.73	0.22	1.83	B'KGND
26	16:48:56	20.	25.4	1.0	0.003	0.027	0.018	0.031	0.1	1.3E+05	5.1E+04	1.15	0.42	0.73	0.19	1.81	B'KGND
27	16:55:27	22.	25.2	1.9	0.003	0.036	0.017	0.022	-0.3	8.8E+04	4.2E+04	1.02	-0.07	1.09	0.31	2.24	B'KGND
28	17:01:58	24.	24.3	2.3	0.002	0.023	0.021	0.040	0.3	1.3E+05	6.8E+04	1.21	0.44	0.77	0.16	1.73	B'KGND
29	17:08:30	26.	24.1	3.3	0.003	0.032	0.018	0.032	1.3	1.0E+05	7.2E+04	1.49	-0.24	1.73	0.31	2.28	B'KGND
30	17:15:02	26.	23.8	3.2	0.001	0.022	0.022	0.037	2.1	1.3E+05	6.8E+04	1.41	0.29	1.12	0.22	1.98	B'KGND
31	17:28:05	25.	24.6	3.3	0.007	0.004	0.276	0.300	8.9	9.3E+05	1.7E+05	1.85	0.36	1.48	0.19	2.03	C TO D
32	17:34:37	25.	24.0	2.9	0.002	0.003	0.344	0.377	6.6	9.5E+05	1.8E+06	3.09	1.67	1.43	0.19	2.11	C TO D
33	17:45:01	27.	23.6	3.3	0.004	0.009	0.566	0.609	11.3	3.9E+06	2.7E+06	28.08	4.73	23.35	0.14	2.33	D TO A
34	17:47:43	26.	23.9	3.2	0.005	0.006	0.475	0.508	10.5	3.8E+06	2.3E+06	6.35	3.47	2.88	0.12	1.94	D TO A
35	17:54:49	26.	23.8	3.0	0.004	0.057	0.320	0.355	15.2	1.9E+06	1.5E+06	11.96	3.38	8.58	0.13	2.10	D TO A
36	18:01:22	28.	24.2	4.4	0.026	0.019	0.566	0.610	38.1	1.9E+06	1.9E+06	32.37	3.47	28.90	0.13	2.28	D TO A
37	18:07:54	27.	24.1	3.9	0.013	0.003	0.522	0.569	15.6	2.0E+06	1.5E+06	8.73	2.27	6.46	0.14	2.11	D TO A
38	18:14:27	29.	23.8	4.6	0.007	0.003	0.389	0.422	8.5	4.6E+06	3.9E+06	12.68	5.89	6.78	0.13	2.25	D TO A
39	18:20:59	28.	23.3	3.9	0.002	0.036	0.200	0.215	6.8	2.9E+06	1.5E+06	5.74	2.62	3.12	0.11	1.98	D TO A

NOTE: See Table 9 pages 18-19 for a description of column headings and units.

Table 23. Experiment No. 8, 27 October 1976 Morning

DATA MAP: VAN SAN BERN 301J /76 PROCESS DATE: 14-JAN-77

RUN#	TIME	RH%	TOUT	DEWPT	SO2	O3	NO	NOX	CO	CNC	ANT	V3-	ENV	VAC	DPO VAC	SO VAC	PASS LABEL
1	6:45:42	34.	13.1	-2.4	0.009	0.003	0.161	0.186	6.0	5.1E+05	3.0E+05	19.91	0.27	19.64	0.22	2.19	B'KGND 1
2	6:52:17	32.	14.8	-1.7	0.022	0.001	0.699	0.730	14.6	5.0E+06	2.5E+06	48.39	7.38	41.01	0.16	2.31	A TO B
3	7:08:41	34.	15.4	-0.2	0.034	0.011	0.940	0.962	17.2	9.4E+06	4.0E+06	86.68	5.48	81.19	0.18	2.08	B TO C
4	7:15:13	32.	15.7	-0.9	0.044	0.005	1.451	1.485	24.9	7.4E+06	3.4E+06	55.25	7.97	47.28	0.15	2.29	B TO C
5	7:21:46	33.	15.3	-0.9	0.035	0.003	1.402	1.469	31.4	7.0E+06	3.1E+06	52.43	8.87	43.56	0.14	2.13	C TO B
6	7:28:18	42.	13.3	0.7	0.043	0.035	1.246	1.301	34.8	7.9E+06	3.3E+06	63.35	9.15	54.20	0.16	2.19	C TO B
7	7:34:51	39.	14.3	0.6	0.043	0.016	1.083	1.132	30.9	4.1E+06	1.7E+06	53.42	3.82	49.60	0.16	2.22	C TO B
8	7:41:23	47.	13.6	2.6	0.068	0.019	1.706	1.799	51.8	5.0E+06	2.5E+06	67.50	5.13	62.37	0.14	2.19	C TO B
9	7:46:26	37.	15.2	0.5	0.051	0.018	1.659	1.711	40.7	9.9E+06	4.0E+06	87.28	9.69	77.59	0.16	2.13	B TO A
10	7:59:31	39.	16.0	2.0	0.012	0.001	0.259	0.294	9.6	4.4E+05	2.5E+05	18.33	1.23	17.10	0.16	1.87	B'KGND 1
11	8:06:03	36.	15.8	0.8	0.021	0.005	0.433	0.478	22.2	1.0E+06	6.9E+05	30.85	2.54	28.31	0.17	2.24	B'KGND 1
12	8:12:35	43.	14.8	2.4	0.013	0.001	0.334	0.371	15.0	4.1E+05	2.1E+05	19.60	2.38	17.22	0.15	1.92	B'KGND 1
13	8:15:18	39.	15.5	1.7	0.014	0.001	0.337	0.373	14.1	4.3E+05	2.5E+05	19.37	2.16	17.21	0.15	1.91	B'KGND 1
14	8:28:55	40.	16.9	3.1	0.043	0.001	1.296	1.379	23.8	9.1E+06	4.0E+06	42.51	9.57	32.94	0.15	2.31	A TO B
15	8:35:27	30.	18.9	0.8	0.051	0.020	1.325	1.400	29.3	7.9E+06	3.6E+06	76.75	4.93	71.82	0.18	2.22	B TO C
16	8:41:59	32.	18.3	1.5	0.031	0.003	1.021	1.096	22.8	4.0E+06	3.6E+06	73.72	9.90	63.82	0.14	2.25	B TO C
17	8:48:31	30.	19.1	1.1	0.042	0.001	1.071	1.142	19.1	7.5E+06	3.9E+06	48.52	11.83	36.70	0.16	2.00	B TO C
18	8:55:03	27.	19.8	0.5	0.041	0.011	1.284	1.374	23.5	8.3E+06	3.3E+06	49.19	4.24	44.96	0.18	2.34	C TO D
19	9:01:35	27.	19.7	0.3	0.034	0.001	1.129	1.212	23.4	6.5E+06	2.6E+06	41.24	6.57	34.67	0.17	2.12	C TO D
20	9:10:49	34.	20.7	4.2	0.044	0.005	1.030	1.130	27.4	5.8E+06	2.5E+06	59.10	5.46	53.64	0.19	2.00	D TO E
21	9:17:55	23.	21.0	-1.1	0.058	0.001	0.734	0.812	14.4	5.5E+06	1.4E+06	55.63	0.50	55.13	0.21	2.13	D TO E
22	9:50:36	27.	20.9	1.1	0.004	0.008	0.096	0.152	3.6	1.4E+05	6.7E+04	9.09	0.53	8.57	0.19	2.06	B'KGND 2
23	9:57:08	27.	21.5	1.6	0.003	0.008	0.070	0.120	3.1	1.4E+05	7.3E+04	9.16	0.41	8.75	0.19	2.10	B'KGND 2
24	10:03:40	30.	21.2	2.9	0.004	0.012	0.063	0.122	2.3	1.2E+05	6.6E+04	7.64	0.33	7.31	0.18	2.00	B'KGND 2
25	10:10:12	30.	21.6	3.3	0.009	0.014	0.064	0.120	2.5	1.6E+05	8.6E+04	9.29	0.53	8.76	0.19	2.05	B'KGND 2
26	10:16:44	32.	22.0	4.7	0.006	0.014	0.060	0.116	2.3	1.3E+05	8.1E+04	8.92	0.40	8.52	0.20	2.07	B'KGND 2
27	10:19:26	37.	21.8	6.4	0.010	0.016	0.062	0.119	2.3	1.3E+05	7.6E+04	9.36	0.60	8.77	0.20	2.07	B'KGND 2
28	10:26:32	35.	22.8	6.6	0.004	0.015	0.059	0.105	1.7	1.4E+05	8.9E+04	8.43	0.36	8.07	0.18	1.97	B'KGND 2
29	10:33:04	35.	22.8	6.4	0.004	0.010	0.109	0.163	2.3	6.3E+05	1.1E+05	9.89	0.64	9.25	0.17	1.95	B'KGND 2
30	10:39:37	38.	23.1	8.0	0.006	0.013	0.065	0.126	2.5	2.1E+05	9.9E+04	10.29	0.60	9.69	0.19	2.10	B'KGND 2
31	10:46:09	35.	23.2	6.8	0.007	0.009	0.068	0.127	2.4	1.4E+05	9.4E+04	9.84	0.52	9.32	0.20	2.05	B'KGND 2
32	10:52:40	38.	23.1	8.0	0.008	0.010	0.078	0.145	2.7	1.5E+05	1.0E+05	11.90	0.89	11.01	0.20	2.00	B'KGND 2

NOTE: See Table 9 pages 18-19 for a description of column headings and units.

Table 24. Experiment No. 9, 27 October 1976 Afternoon

DATA MAP: VAN VENTURA 301J /76 PROCESS DATE: 14-JAN-77

RUN#	TIME	RH%	TOUT	DEWPT	SO2	O3	NO	NOX	CO	CNC	ANT	V3-	ENV	VAC	DPO VAC	SO VAC	PASS LABEL
1	13:43:34	23.	25.2	2.3	0.014	0.085	0.224	0.278	20.5	1.8E+06	1.6E+06	34.28	5.02	29.26	0.12	2.57	A TO B
2	13:50:08	19.	27.8	1.9	0.007	0.005	0.317	0.412	9.8	6.0E+06	2.0E+06	21.07	3.40	17.67	0.18	2.32	A TO B
3	13:56:41	20.	28.8	3.4	0.003	0.005	0.338	0.368	5.9	5.6E+06	1.4E+06	6.72	3.41	3.31	0.11	1.97	A TO B
4	14:03:13	19.	29.1	3.2	0.009	0.010	0.547	0.572	22.0	4.9E+06	1.0E+06	12.25	3.13	9.12	0.19	1.93	A TO B
5	14:09:46	21.	27.7	3.3	0.004	0.024	0.033	0.042	1.5	2.9E+05	4.5E+04	1.19	0.76	0.43	0.10	1.52	A TO B
6	14:12:28	18.	28.7	2.2	0.005	0.011	0.270	0.311	5.4	3.6E+06	1.2E+06	3.48	1.92	1.56	0.18	1.68	A TO B
7	14:22:18	20.	27.2	2.4	0.003	0.015	0.542	0.559	7.2	8.5E+06	2.9E+06	14.20	3.93	10.27	0.18	2.98	B TO C
8	14:29:22	21.	27.6	3.1	0.015	0.005	0.653	0.708	10.6	5.9E+06	1.6E+06	13.35	4.13	9.22	0.15	2.24	B TO C
9	14:35:53	21.	28.6	4.1	0.020	0.001	0.828	0.884	13.3	9.4E+06	3.0E+06	11.64	5.83	5.81	0.15	2.15	B TO C
10	14:42:25	20.	29.1	3.8	0.029	0.046	0.886	0.926	19.2	9.4E+06	2.6E+06	19.74	5.61	14.13	0.16	2.12	B TO C
11	14:48:55	24.	27.5	5.0	0.022	0.004	0.320	0.393	8.1	5.1E+06	1.5E+06	16.39	3.16	13.24	0.17	2.17	C TO D
12	14:53:49	19.	28.9	3.1	0.013	0.023	0.658	0.704	6.1	5.7E+06	9.4E+05	38.91	4.40	34.51	0.16	2.46	C TO D
13	15:00:20	19.	29.2	2.9	0.025	0.019	1.053	1.096	19.0	7.4E+06	2.3E+06	40.99	5.72	35.27	0.12	2.11	C TO D
14	15:19:52	14.	27.2	-2.3	0.006	0.042	0.011	0.015	0.7	7.3E+04	2.2E+04	1.79	0.17	1.62	0.23	2.16	B'KGND
15	15:26:24	15.	27.1	-2.1	0.002	0.040	0.013	0.019	-0.7	7.6E+04	2.8E+04	1.36	0.30	1.06	0.19	1.90	B'KGND
16	15:32:54	19.	27.1	1.2	0.002	0.044	0.009	0.013	-0.8	6.9E+04	2.4E+04	1.45	0.29	1.16	0.22	1.95	B'KGND
17	15:39:25	21.	27.0	2.7	0.003	0.027	0.015	0.022	-0.8	1.1E+05	3.5E+04	1.67	0.32	1.35	0.21	1.98	B'KGND
18	15:45:55	22.	27.3	4.0	0.005	0.039	0.016	0.023	-0.5	1.0E+05	4.5E+04	1.82	0.10	1.72	0.25	2.22	B'KGND
19	15:52:26	22.	27.2	3.4	0.002	0.044	0.009	0.015	-0.8	8.0E+04	2.9E+04	1.84	-0.05	1.90	0.27	2.16	B'KGND
20	15:58:57	19.	27.5	1.9	0.002	0.049	0.011	0.018	-0.8	8.1E+04	3.6E+04	2.42	-0.37	2.79	0.32	2.12	B'KGND
21	16:05:28	21.	27.5	3.2	0.003	0.032	0.011	0.019	-0.6	1.1E+05	4.2E+04	2.27	-0.10	2.37	0.28	2.15	B'KGND
22	16:11:59	20.	28.0	3.0	0.003	0.042	0.031	0.044	2.6	2.4E+05	4.7E+04	2.45	0.46	1.99	0.22	1.95	B'KGND
23	16:22:01	20.	27.8	3.1	0.003	0.033	0.014	0.025	-0.3	9.0E+04	5.9E+04	1.68	0.14	1.55	0.26	2.26	B'KGND
24	16:28:32	13.	27.6	-3.7	0.003	0.048	0.010	0.014	-0.8	6.7E+04	4.6E+04	2.09	0.23	1.86	0.29	2.05	B'KGND
25	16:41:34	18.	28.0	1.7	0.013	0.027	1.187	1.221	25.2	7.5E+06	1.9E+06	7.92	3.06	4.86	0.16	2.53	D TO E
26	16:48:05	20.	27.2	2.0	0.002	0.013	0.138	0.167	6.2	1.9E+06	9.4E+05	6.59	2.31	4.29	0.12	1.95	D TO E
27	16:54:36	21.	27.3	2.8	0.006	0.022	0.727	0.746	10.5	8.3E+06	3.2E+06	9.35	5.36	3.98	0.19	2.53	D TO E
28	17:01:06	19.	26.7	1.2	0.001	0.046	0.035	0.039	1.6	1.2E+06	4.5E+05	3.60	1.60	2.00	0.13	2.00	D TO E
29	17:07:37	11.	26.2	-7.1	0.001	0.008	0.313	0.344	4.6	4.3E+06	1.3E+06	5.50	2.94	2.57	0.12	1.94	E TO F
30	17:14:08	14.	26.6	-3.4	0.004	0.008	0.753	0.770	14.0	6.7E+06	3.4E+06	16.07	6.15	9.91	0.16	2.19	E TO F
31	17:20:39	17.	27.0	-0.3	0.030	0.020	0.701	0.732	26.7	4.3E+06	1.6E+06	23.05	3.59	19.46	0.15	2.43	E TO F
32	17:27:09	15.	27.1	-2.2	0.034	0.033	1.163	1.214	40.9	4.8E+06	2.5E+06	23.84	5.76	18.08	0.13	2.41	E TO F
33	17:33:39	16.	26.9	-1.2	0.025	0.001	0.847	0.881	20.1	5.7E+06	1.8E+06	17.87	4.72	13.15	0.12	2.23	E TO F
34	18:10:34	30.	23.1	4.7	0.019	0.015	0.928	0.987	16.1	7.2E+06	3.1E+06	26.10	4.24	21.86	0.17	2.49	G TO H
35	18:17:06	35.	21.9	5.7	0.032	0.019	1.137	1.203	17.6	8.5E+06	2.8E+06	40.84	7.93	32.92	0.12	2.11	H TO I

NOTE: See Table 9 pages 18-19 for a description of column headings and units.

Table 25. Experiment No. 10, 28 October 1976 Afternoon

DATA MAP: VAN LACS 302J /76 PROCESS DATE: 14-JAN-77

RUN#	TIME	RH%	TOUT	DEWPT	SO2	O3	NO	NOX	CO	CNC	ANT	V3-	ENV	VAC	DPO VAC	SO VAC	PASS LABEL
1	15:57:29	52.	23. 5	13. 1	0. 001	0. 053	0. 009	0. 019	-7. 2	1. 7E+05	5. 1E+04	4. 31	0. 29	4. 01	0. 21	2. 05	B'KGND
2	16:04:02	55.	24. 0	14. 3	0. 001	0. 056	0. 008	0. 021	-11. 9	1. 7E+05	6. 5E+04	4. 50	0. 25	4. 25	0. 21	1. 98	B'KGND
3	16:10:35	53.	23. 9	13. 8	0. 001	0. 052	0. 008	0. 022	-2. 5	1. 8E+05	5. 6E+04	4. 80	0. 07	4. 74	0. 22	2. 02	B'KGND
4	16:17:08	51.	23. 3	12. 7	0. 002	0. 054	0. 010	0. 020	-2. 0	1. 7E+05	4. 3E+04	3. 83	-0. 03	3. 86	0. 22	2. 12	B'KGND
5	16:23:40	52.	23. 3	12. 8	0. 001	0. 054	0. 009	0. 017	-1. 8	1. 7E+05	3. 7E+04	4. 10	0. 51	3. 60	0. 19	1. 65	B'KGND
6	16:30:12	44.	22. 6	9. 7	0. 002	0. 061	0. 006	0. 015	-1. 7	1. 7E+05	5. 2E+04	4. 14	0. 17	3. 97	0. 21	1. 95	B'KGND
7	16:36:44	62.	22. 5	15. 0	0. 002	0. 051	0. 010	0. 026	-0. 9	1. 2E+05	4. 5E+04	4. 40	0. 23	4. 18	0. 21	1. 98	B'KGND
8	16:43:16	62.	22. 5	14. 9	0. 001	0. 058	0. 008	0. 017	-1. 4	9. 1E+04	4. 5E+04	4. 35	0. 25	4. 10	0. 21	1. 95	B'KGND
9	16:49:50	67.	22. 5	16. 1	0. 001	0. 057	0. 008	0. 018	-1. 2	9. 3E+04	3. 7E+04	4. 51	0. 48	4. 02	0. 20	1. 83	B'KGND
10	16:56:20	56.	22. 1	13. 0	0. 001	0. 056	0. 006	0. 021	-1. 1	1. 0E+05	1. 1E+05	1. 87	0. 47	1. 41	0. 11	1. 91	B'KGND
11	17:06:08	54.	22. 2	12. 4	0. 001	0. 053	0. 007	0. 023	-1. 1	1. 1E+05	4. 3E+04	4. 59	0. 24	4. 35	0. 21	1. 92	B'KGND
12	17:12:40	45.	22. 8	10. 2	0. 001	0. 035	0. 010	0. 030	1. 5	2. 5E+05	4. 0E+05	9. 68	1. 14	8. 54	0. 21	2. 20	B'KGND
13	17:45:18	49.	23. 1	11. 9	0. 017	0. 020	0. 341	0. 389	18. 5	4. 0E+06	1. 9E+06	25. 96	1. 96	24. 00	0. 14	2. 55	A TO B
14	17:51:50	51.	23. 0	12. 4	0. 012	-0. 000	0. 420	0. 480	14. 7	5. 5E+06	8. 5E+05	13. 29	2. 97	10. 31	0. 15	2. 17	A TO B
15	17:58:21	50.	23. 8	12. 6	0. 031	0. 014	0. 952	1. 021	33. 5	7. 7E+06	2. 3E+06	21. 13	2. 82	18. 31	0. 14	2. 52	B TO C
16	18:04:52	47.	23. 7	11. 7	0. 022	-0. 000	0. 444	0. 518	25. 0	3. 4E+06	1. 2E+06	27. 89	0. 32	27. 57	0. 15	2. 40	B TO C
17	18:11:23	44.	22. 5	9. 5	0. 013	-0. 000	0. 442	0. 512	8. 8	6. 1E+06	4. 5E+05	16. 29	1. 22	15. 07	0. 14	2. 07	B TO C
18	18:17:55	56.	22. 3	13. 2	0. 030	0. 002	0. 655	0. 754	27. 3	3. 7E+06	1. 5E+06	34. 94	5. 72	29. 22	0. 13	2. 18	B TO C
19	18:24:26	53.	22. 3	12. 2	0. 121	0. 045	0. 754	0. 828	46. 4	4. 2E+06	3. 2E+06	37. 42	5. 20	32. 22	0. 16	2. 37	B TO C
20	18:30:58	24.	24. 3	2. 2	0. 023	0. 001	0. 642	0. 693	10. 1	4. 0E+06	2. 9E+06	22. 62	4. 87	17. 75	0. 18	2. 26	B TO C
21	18:37:30	24.	23. 5	1. 5	0. 001	0. 011	0. 264	0. 302	9. 8	1. 8E+06	3. 6E+05	7. 61	1. 84	5. 77	0. 12	1. 90	C TO A

NOTE: See Table 9 pages 18-19 for a description of column headings and units.

Table 26. Experiment No. 12, 30 October 1976 Mini-Method

DATA MAP: VAN FOOTHILL 304J/76 PROCESS DATE: 15-FEB-77

RUN#	TIME	RH%	TOUT	DEWPT	SO2	O3	NO	NOX	CO	CNC	ANT	V3-	ENV	VAC	DPO VAC	SQ VAC	PASS LABEL
1	3:21:04	53.	11.9	2.6	0.003	-0.000	0.032	0.081	3.9	1.1E+05	1.4E+05	14.81	-0.92	15.73	0.27	1.85	B'KGND
2	3:27:40	40.	11.4	0.7	0.003	0.023	0.015	0.045	2.0	4.5E+04	7.5E+04	9.23	-0.04	9.26	0.25	1.81	B'KGND
3	3:30:22	55.	10.7	2.0	0.003	0.025	0.032	0.060	1.9	7.7E+04	3.0E+04	7.82	-0.29	8.11	0.26	1.80	B'KGND
4	3:44:04	47.	11.2	0.3	0.003	0.019	0.017	0.055	1.6	3.1E+05	1.5E+05	10.50	0.50	10.00	0.27	1.84	B'KGND
5	3:50:36	65.	10.5	4.2	0.004	0.004	0.039	0.093	3.5	1.1E+06	3.9E+05	16.59	-0.89	17.48	0.28	1.83	B'KGND
6	3:57:09	65.	11.9	5.6	0.004	0.002	0.045	0.106	3.4	3.9E+05	2.1E+05	17.74	-0.45	18.19	0.31	1.86	B'KGND
7	4:03:41	70.	12.2	8.5	0.002	-0.000	0.272	0.321	4.3	3.5E+06	1.1E+06	29.34	0.72	28.62	0.29	1.80	B'KGND
8	4:10:13	50.	14.1	3.9	0.002	0.026	0.026	0.064	2.4	3.7E+05	2.0E+05	17.94	1.44	16.49	0.28	1.82	B'KGND
9	4:16:45	74.	11.9	7.5	0.003	-0.000	0.053	0.093	2.3	6.7E+05	5.6E+05	18.28	1.00	17.28	0.30	1.82	B'KGND
10	4:23:16	74.	11.9	7.5	0.002	0.001	0.193	0.259	4.8	2.9E+06	7.8E+05	20.69	1.69	19.00	0.28	1.84	B'KGND
11	4:29:48	70.	8.9	3.8	0.003	-0.000	0.033	0.082	1.8	6.0E+05	3.3E+05	12.34	0.63	11.71	0.29	1.88	B'KGND
12	4:36:20	50.	11.2	1.1	0.003	0.014	0.023	0.052	0.8	2.5E+05	6.0E+04	6.26	-0.15	6.42	0.28	1.84	TURN
13	4:42:51	64.	9.6	3.1	0.003	-0.000	0.022	0.052	1.0	2.5E+05	5.1E+04	11.29	-0.40	11.69	0.20	1.81	B'KGND
14	5:22:47	71.	10.4	5.4	0.014	-0.000	0.269	0.317	6.1	6.9E+06	1.9E+06	20.22	5.72	14.50	0.21	2.14	A TO C
15	5:29:21	62.	9.8	2.0	0.003	-0.000	0.357	0.400	3.4	8.2E+06	3.0E+06	15.13	6.39	8.73	0.20	2.20	A TO C
16	5:35:54	53.	11.2	2.0	0.003	0.008	0.245	0.297	3.3	4.7E+06	1.7E+06	17.07	4.50	12.57	0.13	2.45	A TO C
17	5:42:27	40.	11.4	0.7	0.002	0.004	0.200	0.337	2.1	6.6E+06	1.7E+06	12.32	2.73	9.59	0.22	2.23	C TO D
18	5:48:59	57.	10.6	2.4	0.004	0.002	0.149	0.197	1.7	3.6E+06	1.5E+06	11.23	1.99	9.25	0.24	2.18	C TO D
19	5:55:33	70.	12.0	6.6	0.006	-0.000	0.428	0.490	7.5	8.3E+06	2.9E+06	22.01	3.91	18.10	0.22	2.16	C TO D
20	6:02:05	70.	11.9	6.7	0.004	0.002	0.480	0.541	4.1	9.5E+06	2.9E+06	25.68	4.45	21.23	0.22	2.05	C TO D
21	6:04:47	45.	13.1	1.5	0.038	0.013	0.604	0.658	8.7	7.3E+06	1.8E+06	11.75	3.26	8.49	0.21	2.09	C TO D
22	6:11:53	73.	11.9	7.3	0.007	0.011	0.400	0.468	0.0	5.0E+06	1.4E+06	24.33	2.01	22.31	0.24	1.89	D TO A
23	6:17:34	73.	11.1	6.4	0.014	-0.000	0.668	0.727	5.1	7.4E+06	2.4E+06	35.00	5.94	29.06	0.19	2.29	D TO A

NOTE: See Table 9 pages 18-19 for a description of column headings and units.

data are given in Table 27. The meaning of the mnemonics is given in Table 9. The ENV column gives an estimate of the aerosol volume in the nuclei mode. It is calculated by subtracting VAC from V3-, and subject to considerable error when it has a value smaller than about 10% of V3-.

For reasons described in Section 3.6, the runs on 21 October and 26 October have been selected for special analysis. Therefore, freeway and background concentration averages for these days are given in Tables 28 and 29.

Aerosol difference size distributions have been calculated at the University of Minnesota, and are shown in Figures 8 through 12. Figure 13 gives the aerosol size distributions measured on 30 October, and Figure 14 gives the difference distribution for this experiment. The difference distributions were obtained by averaging together the size distributions obtained on the freeway during the indicated run, and then subtracting the average size distribution observed at the background site during the same time period. The error bars give the range of values observed on the freeway. By comparison, the errors due to fluctuations in the data taken at the background sites are negligible. Figure 15 gives a grand average freeway aerosol size distribution which was obtained by combining the data for the runs indicated in this figure.

To obtain information on the fraction of vehicles on the road which were equipped with catalysts, sample counts were taken by an observer in the University of Minnesota van on some of the experiments. These counts were primarily based on the license plate numbers and are reported in Table 30.

Cars registered during the 1975 model year and thereafter (the catalyst equipped cars) were issued yellow on blue license plates with a leading alphabetic character of M, N, or higher in the alphabet. For example, the following license plate numbers were issued to 1975 or newer cars: 123 MXX, 123 NXX, 123 OXX, etc., where 123 represents any combination of numbers from 0 to 9, and XX represents any combination of alphabetic characters from A to Z. Cars with all other license plate configurations (yellow on blue license plates with such numbers as: 123 AXX, 123 BXX, ... 123 LXX, and all yellow on black license plates) were counted as non-catalyst equipped.

Heavy duty and light duty trucks, tax exempt vehicles, motorcycles, and non-California vehicles were omitted from the sample population. Also, cars that were purchased outside California and re-registered after 1975 may have license plate numbers within the same range as catalyst equipped cars, but this was taken into account on the basis of the vehicle description.

Table 27. Average Daily Values for In-Roadway (F) and Background (B) Concentrations and the In-Roadway Increment (Δ)

Date	Experiment Number		Site	Measured Species												
				SO_2	O_3	NO	NO_x	CO	ANC	V3-	* VAN	DPG VAN	SG VAN	VAC	DPG VAC	SG VAC
20 Oct 76	2	294	F	0.034	0.009	0.772	0.896	21.5	4.8E6	29.9	10.5	0.029	1.7	28.2	0.20	1.9
			B	0.020	0.030	0.031	0.114	4.6	2.9E5	6.5	1.0	0.039	1.8	11.7	0.23	1.8
			Δ	0.014	-0.020	0.741	0.782	16.9	4.5E6	23.4	11.0	0.030	1.7	15.2	0.17	1.9
21 Oct 76	3	295	F	0.031	0.006	0.681	0.749	19.2	4.5E6	27.1	12.1	0.030	1.7	16.2	0.14	1.7
			B	0.008	0.019	0.028	0.050	0.8	1.8E5	2.9	0.4	0.036	1.8	2.6	0.20	1.8
			Δ	0.023	-0.013	0.653	0.699	18.4	4.3E6	24.2	10.9	0.030	1.7	15.2	0.13	1.8
26 Oct 76	7	300	F	0.008	0.015	0.507	0.543	12.2	1.9E6	13.4	4.1	0.021	1.6	8.3	0.20	2.0
			B	0.003	0.038	0.017	0.025	0.2	1.1E5	1.1	0.1	0.029	1.7	0.9	0.28	1.9
			Δ	0.005	-0.023	0.490	0.518	12.0	1.8E6	12.3	4.0	0.021	1.6	7.4	0.19	1.9
27 Oct 76	8	301A	F	0.043	0.009	1.190	1.258	26.9	6.9E6	60.1	18.8	0.033	1.8	46.8	0.20	1.9
			B	0.008	0.009	0.145	0.195	5.9	3.1E5	15.5	1.4	0.055	1.9	8.4	0.21	1.9
			Δ	0.035	0.000	1.045	1.063	21.0	6.6E6	44.6	14.1	0.033	1.8	38.3	0.20	1.9
27 Oct 76	9	301B	F	0.014	0.019	0.608	0.648	13.8	5.6E6	17.3	6.4	0.028	1.7	10.4	0.20	2.0
			B	0.003	0.040	0.014	0.021	-0.3	9.9E4	1.9	0.3	0.036	1.8	1.7	0.28	2.0
			Δ	0.011	-0.021	0.594	0.627	14.1	5.5E6	15.4	6.1	0.03	1.7	8.5	0.18	1.9
28 Oct 76	10	302	F	0.030	0.010	0.546	0.611	21.6	4.5E6	23.0	6.7	0.031	1.7	16.5	0.19	2.0
			B	0.001	0.053	0.008	0.021	-2.6	1.5E5	4.6	0.5	0.036	1.8	4.0	0.22	1.9
			Δ	0.029	-0.043	0.538	0.590	24.2	4.3E6	18.4	6.2	0.033	1.8	12.5	0.20	2.0
Grand Averages			$\overline{F}$	0.027	0.011	0.717	0.784	19.2	4.7E6	28.5	9.8	0.029	1.7	21.1	0.19	1.9
			σ	0.013	0.005	0.250	0.263	5.5	1.6E6	16.6	5.3	0.004	0.06	14.4	0.02	0.1
			$\overline{B}$	0.007	0.032	0.041	0.071	1.4	1.9E5	5.4	0.6	0.039	1.8	4.8	0.24	1.9
			σ	0.007	0.016	0.052	0.070	3.2	0.9E5	5.3	0.5	0.009	0.06	4.3	0.04	0.1
			$\overline{\Delta}$	0.020	-0.030	0.676	0.713	17.8	4.5E6	23.2	9.2	-	-	16.3	-	-

*Note: The model parameters are from a preliminary fit to the difference distributions.

Table 28. Means and Standard Deviations of Data from the Santa Monica Freeway, 21 October 1976 Morning

Run No.	SO_2	O_3	NO	NO_x	CO	Label
1-4	0.009±0.001	0.002±0.000	0.035±0.009	0.067±0.010	1.4±0.2	Background
5-19	0.031±0.011	0.006±0.011	0.681±0.190	0.749±0.205	19±6	Freeway
20-24	0.007±0.001	0.032±0.004	0.022±0.001	0.036±0.003	0.3±0.3	Background
Difference	0.023	-0.011	0.653	0.697	18.4	F-B

Run No.	CNC	ANT	$V3^-$	ENV	VAC	Label
1-4	$(0.16\pm0.01) \times 10^6$	$(0.12\pm0.02) \times 10^6$	3.0±1	0.19±0.10	2.8±1.3	Background
5-19	$(4.5\pm1.6) \times 10^6$	$(3.0\pm1.0) \times 10^6$	2.7±13	7±2	20±11	Freeway
20-24	$(0.20\pm0.01) \times 10^6$	$(0.05 \pm 0.01) \times 10^6$	2.8±1	0.1±0.4	2.9±1.4	Background
Difference	4.3×10^6	2.9×10^6	24	7	17	F-B

Table 29. Means and Standard Deviations of Data from the Ventura Freeway, 26 October

Run No.	SO_2	O_3	NO	NO_x	CO	Label
1-4	0.007 ±0.006	0.020±0.010	0.478±0.261	0.52±0.26	8.3±4.5	Freeway
5-14	0.003 ±0.001	0.044±0.003	0.016±0.001	0.02±0.002	-0.1±0.3	Background
15-22	0.009 ±0.007	0.013±0.008	0.635±0.289	0.67±0.30	13.± 5.	Freeway
23-30	0.002 ±0.001	0.030±0.006	0.019±0.002	0.03±0.01	0.7±0.9	Background
31-39	0.008 ±0.007	0.016±0.019	0.406±0.132	0.44±0.14	14.± 10	Freeway
Difference	0.005	-0.021	0.489	0.52	11	F-B

Run No.	CNC	ANT	$V3^-$	ENV	
1-4	$(4.0\pm0.7) \times 10^6$	$(1.8\pm0.5) \times 10^6$	8.6±2	2.8±1.1	Freeway
5-14	$(0.11\pm0.06) \times 10^6$	$(0.03\pm0.01) \times 10^6$	1.0±0.1	0.13±0.16	Background
15-22	$(0.14\pm0.4) \times 10^6$	$(2.6\pm1.1) \times 10^6$	17±11	4.3±2.3	Freeway
23-30	$(0.11\pm0.02) \times 10^6$	$(0.05\pm0.02) \times 10^6$	1.3±0.2	0.26±0.27	Background
31-39	$(2.5\pm1.3) \times 10^6$	$(1.9\pm1.0) \times 10^6$	12±11	3.1±1.6	Freeway
Difference	3.1×10^6	2.1×10^6	11	3.2	F-13

Figure 8. Difference between the in-roadway and background aerosol size distribution observed on 20 October 1976.

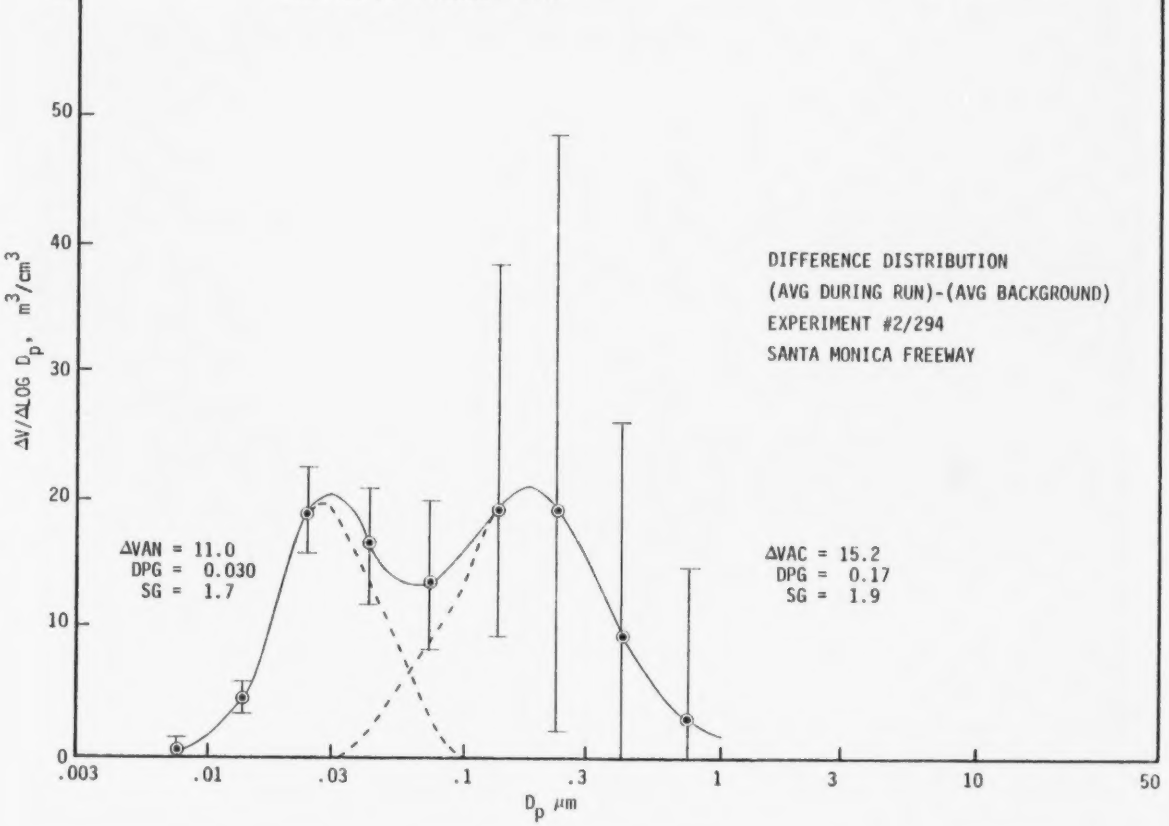
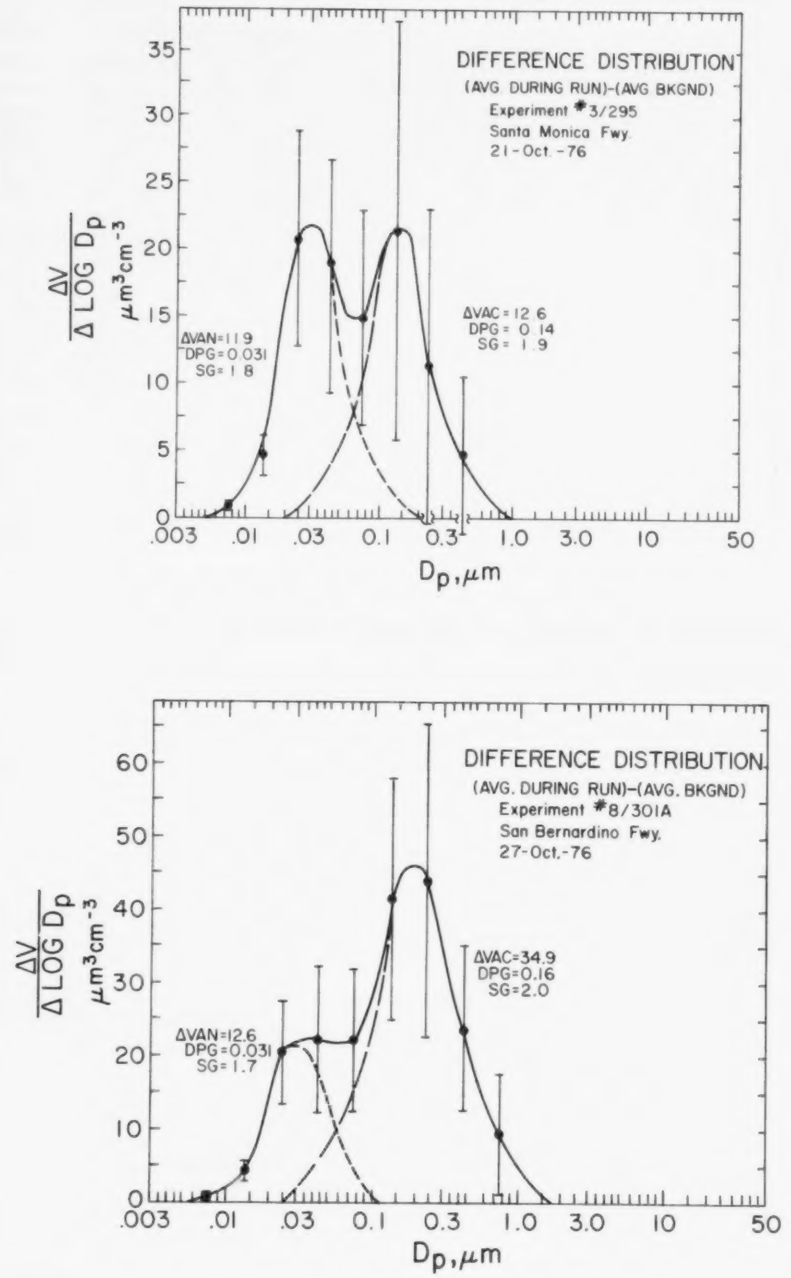


Figure 9.


DIFFERENCE DISTRIBUTION
(AVG DURING RUN)-(AVG BKGND)
Experiment #3/295
Santa Monica Fwy.
21-Oct.-76
ΔVAN=11.9
DPG=0.031
SG=1.8
ΔVAC=12.6
DPG=0.14
SG=1.9
ΔV / Δ LOG Dp
μm3cm-3
35
30
25
20
15
10
5
0
.003
.01
.03
0.1
0.3
1.0
3.0
10
50
Dp, μm
DIFFERENCE DISTRIBUTION
(AVG. DURING RUN)-(AVG. BKGND)
Experiment #8/301A
San Bernardino Fwy.
27-Oct.-76
ΔVAN=12.6
DPG=0.031
SG=1.7
ΔVAC=34.9
DPG=0.16
SG=2.0
ΔV / Δ LOG Dp
μm3cm-3
60
50
40
30
20
10
0
.003
.01
.03
0.1
0.3
1.0
3.0
10
50
Dp, μm

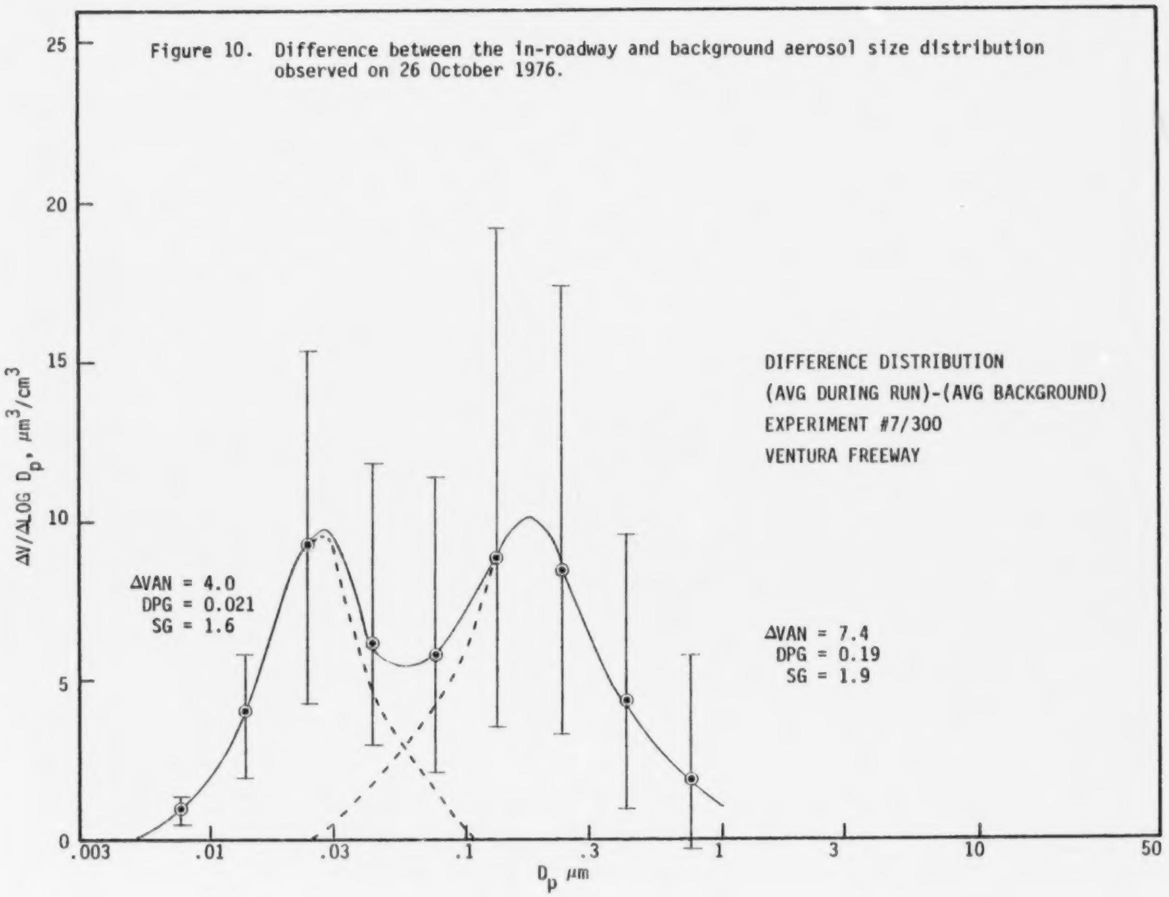


Figure 10. Difference between the in-roadway and background aerosol size distribution observed on 26 October 1976.

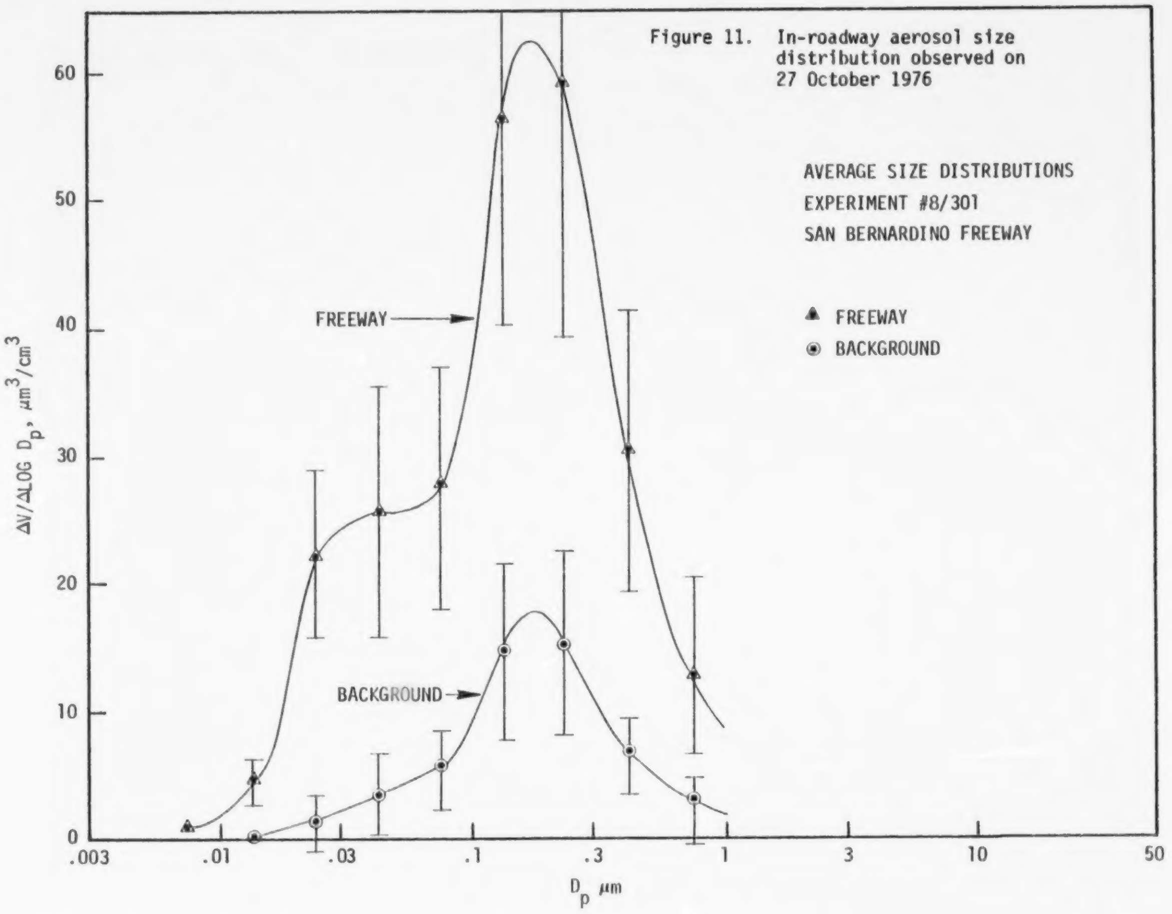
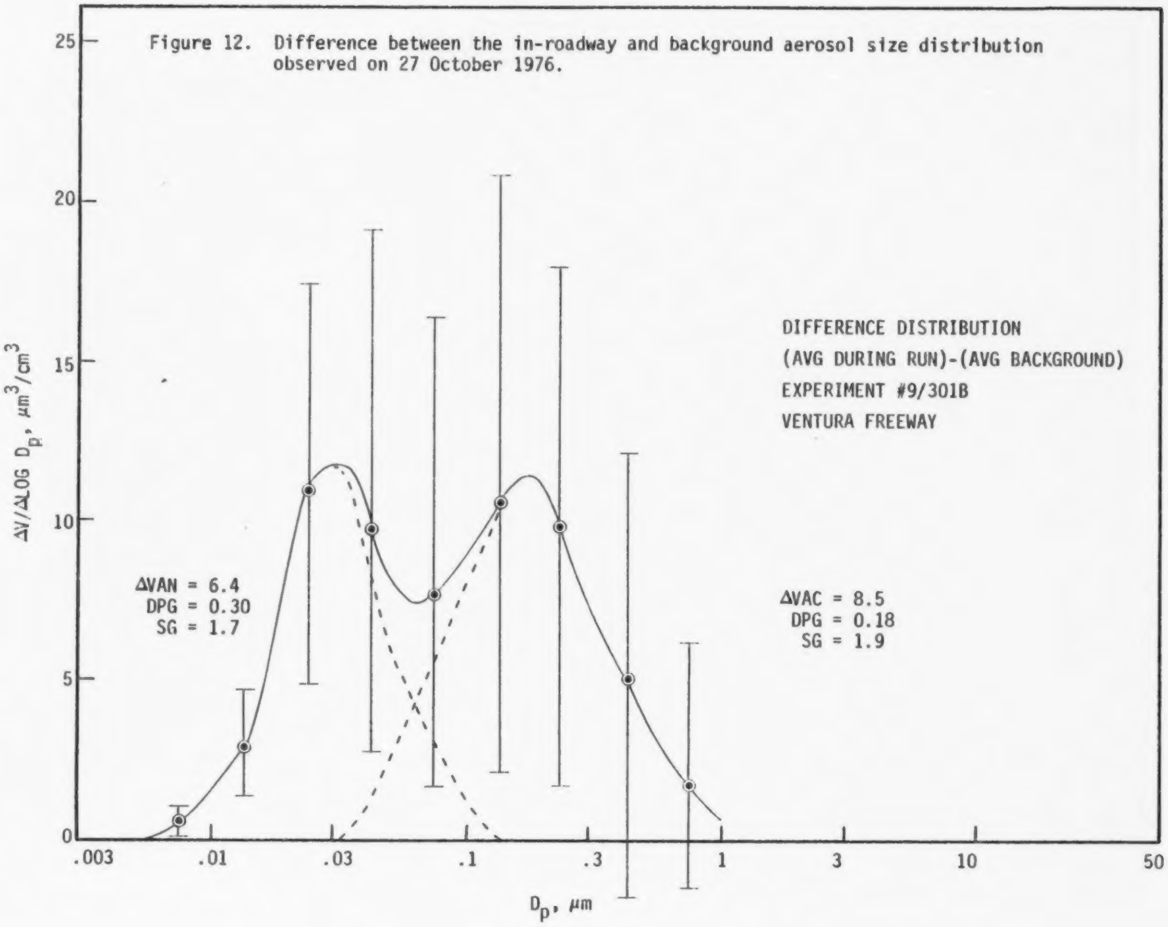


Figure 11. In-roadway aerosol size distribution observed on 27 October 1976

Figure 12. Difference between the in-roadway and background aerosol size distribution observed on 27 October 1976.



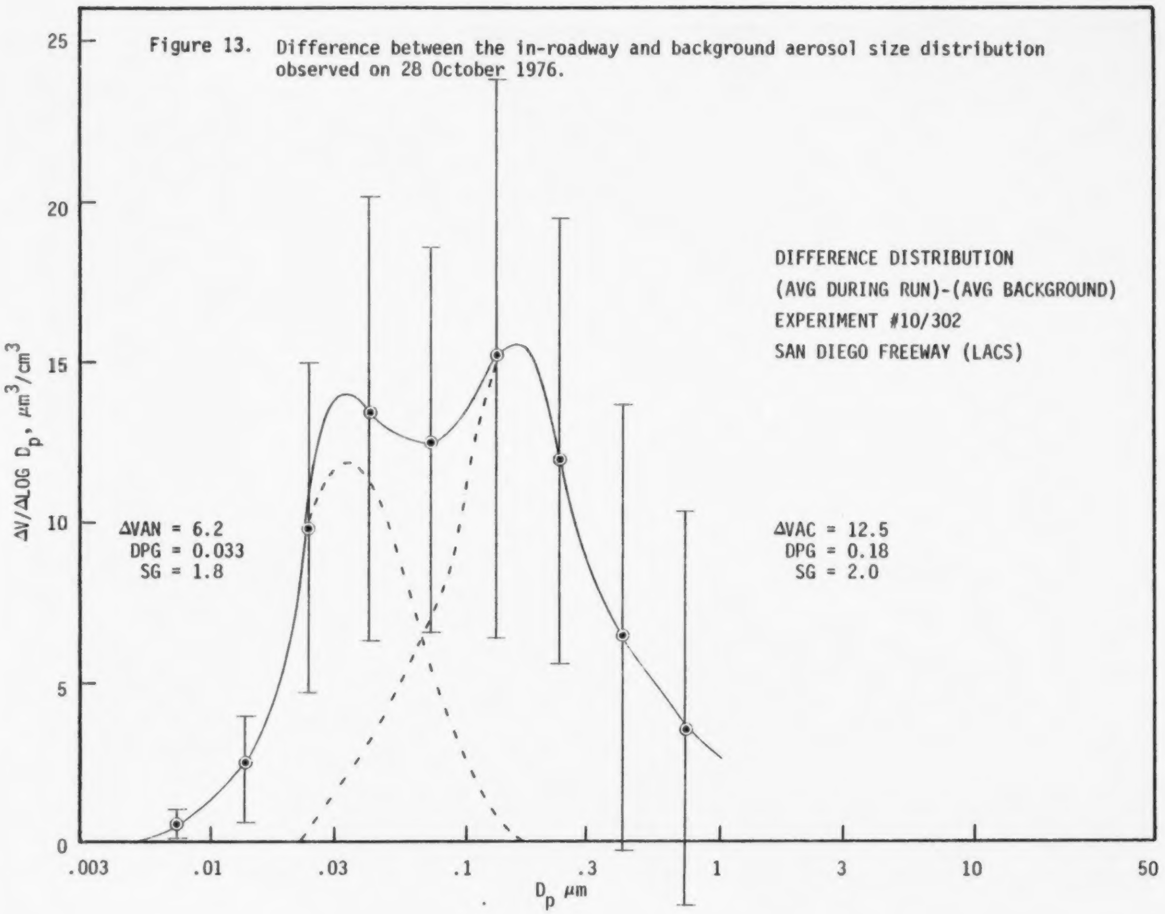


Figure 13. Difference between the in-roadway and background aerosol size distribution observed on 28 October 1976.

Figure 14. In-roadway and background aerosol size distributions observed on 30 October when following several catalyst-equipped cars.

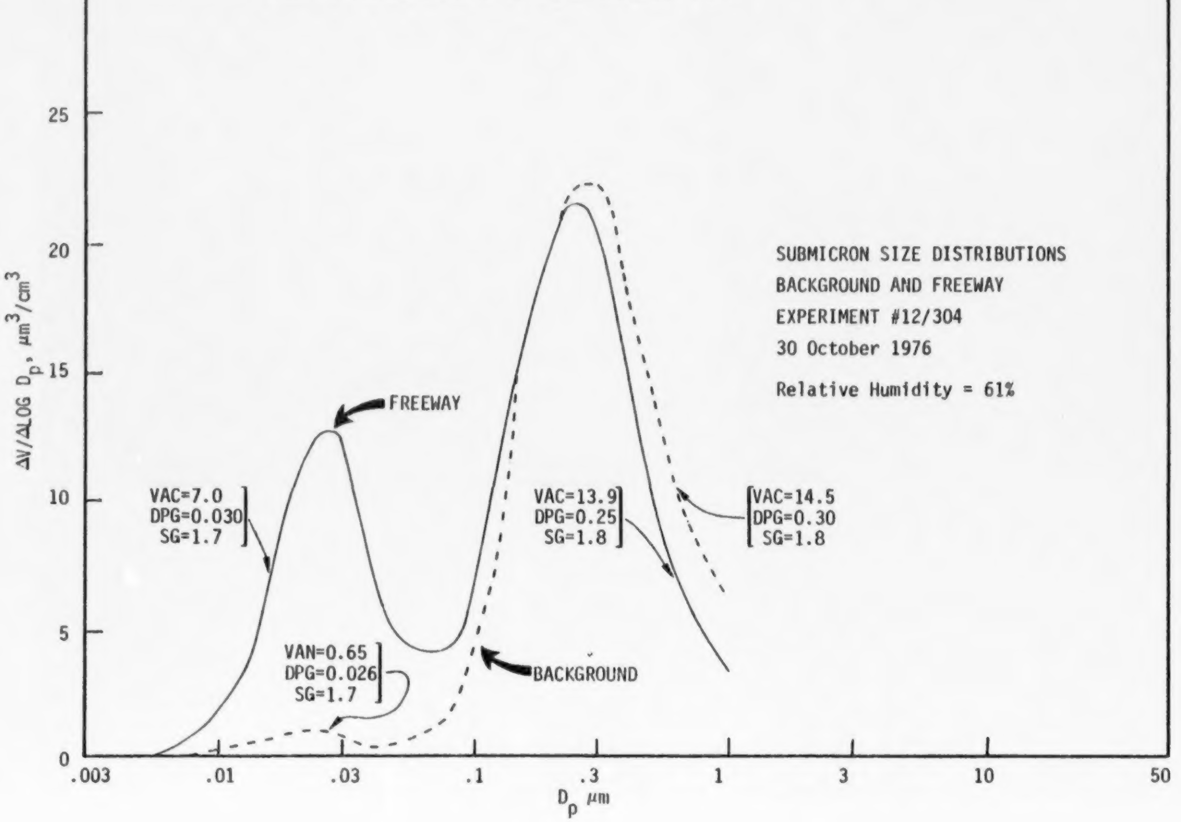


Figure 15. Difference between the in-roadway and background aerosol size distribution observed on 30 October when following several catalyst-equipped cars.

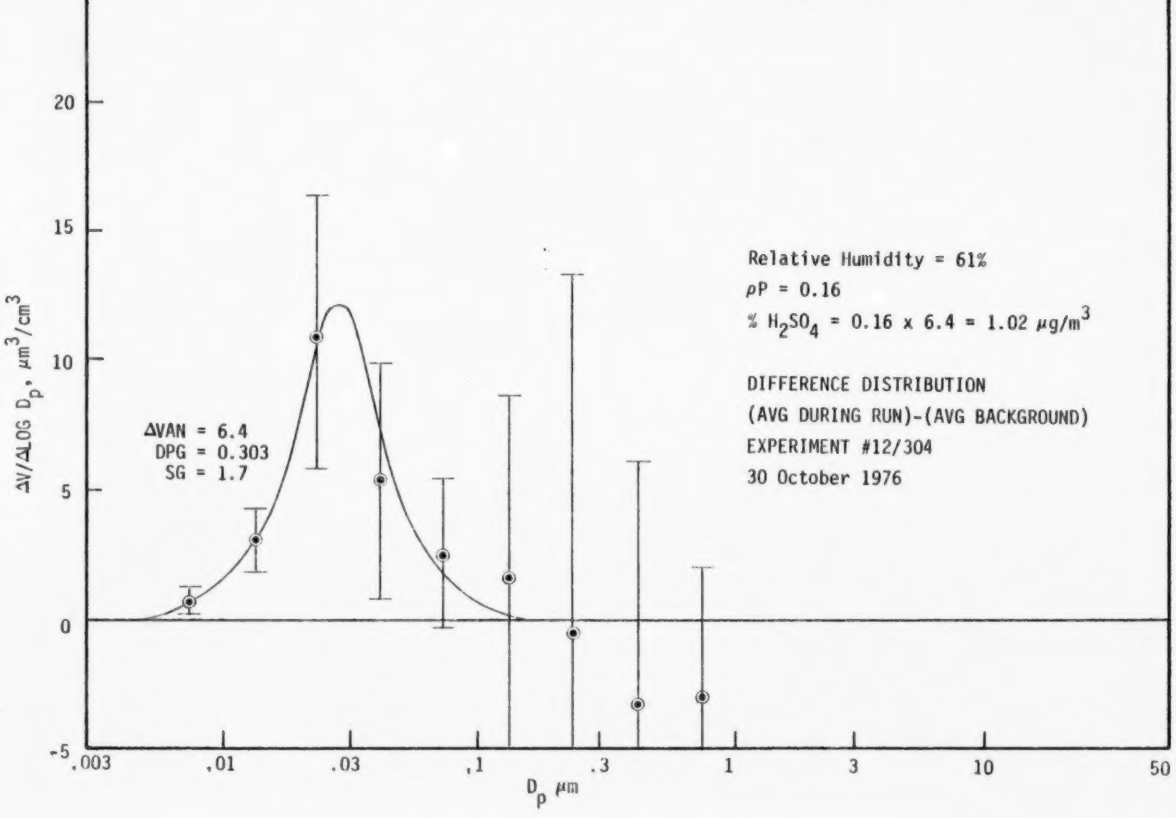


Table 30. Counts of Samples of Cars in Lanes Near the U. Minn.

Van to Determine the Fraction Equipped with Catalysts

(Based on License Plate Leading Letters)

Date	Pass Label	Pass #	Car Count Non-Catalyst	Catalyst	Total	% Catalyst Cars Cars
26 October	C to D	4	44	15	59	25
	E to F	5	96	31	127	24
	F to C	6	55	32	87	37
	C to D	8	96	37	133	28
	D to A	9	164	68	232	29
	D to A 2nd Half	9	95	46	141	33
	Ventura Fwy. Total		550	229	779	29
27 October Morning	A to B	1	51	10	61	16
	B to C	2	100	27	127	21
	C to D	3	96	21	117	18
	Sub Total-Early Morning Runs		247	58	305	18
	A to B	6	78	27	105	26
	B to C	7	75	29	104	28
	C to D	8	99	32	131	24
	D to E	9	35	15	50	30
	Sub Total-Late Morning Runs		281	103	390	27
	San Bernadino Fwy. Total		534	161	695	23
27 October Afternoon	A to B	1	109	49	158	31
	B to C	2	117	54	171	32
	C to D	3	80	33	113	29
	Sub Total-First Ventura Run		306	136	442	31
	D to E	5	72	41	113	36
	E to F	6	122	42	164	26
			194	83	277	30
	Ventura Fwy. Total		500	219	719	31
28 October	A to B	2	72	29	101	29
	B to C	3	65	41	106	39
	C to A	4	62	29	91	32
	San Diego Fwy. Total		179	99	298	33

2.4 THE WASHINGTON UNIVERSITY DATA

The Washington University participants in the October, 1976 field program were associated with Professor E. S. Macias. Their main activity was to operate an instrumented automobile on the freeways and at the background sites. The Washington University car and the University of Minnesota van operated as a team, and generally followed the same schedules and itineraries. The sampling schedule followed by the Washington University car is given in Table 31. The comparison of this schedule with that of the University of Minnesota van is given in Table 32.

The instrumentation in the automobile is shown schematically in Figure 16 and included a TWOMASS sampler, a LBL dichotomous sampler, and an aerosol charger, and a second charger with the capability of adding ammonia to the sampler air flow and passing the sample through a temperature programmed heated tube. The LBL sampler used an air intake outside the car from 19 to 22 October, and sampled from inside the car with the windows open from 24 to 30 October. The TWOMASS sampler and the charger always sampled outside air.

The TWOMASS sampler separates particles into two size fractions (Macias and Husar, 1976). Coarse particles are impacted on a glass fiber filter; the remaining particles are collected on an identical high-efficiency glass fiber filter. Samples were collected on a portion (0.03 cm^2) of a light weight (1.2 mg/cm^2) low pressure drop glass-fiber filter (Pallflex E70) with a consistent and low sulfur blank (0.3 to 0.5 ug/cm^2). The single stage impactor head has a 4.5 mm diameter inlet aperature with a 4.5-mm jet to plate distance. The impactor was designed to have 50% efficiency for 3.5 um particles. This cutoff size was chosen as a compromise between the proper separation of the two modes of the atmospheric aerosol size distribution and the simulation of the aerosol removal characteristics of the human upper respiratory system.

Analysis of water soluble particulate sulfur collected in 2 hr intervals with the TWOMASS sampler was performed using a flash vaporization-flame photometric detector method (Husar, Husar, Macias, Wilson, Durham, Shepard, and Anderson, 1976). The analyzing system consisted of a flash vaporization vessel, flame-photometric detector, integrator and a capacitor discharge across a tungsten boat, resulting in resistance heating to 1100 deg C. Vaporized gaseous decomposition products of sulfur compounds were carried to the flame-photometric detector by a stream of clean, charcoal filtered air at a flow rate of 2 cm^3/sec. The detector used was the Meloy SA-160 flame photometric total sulfur sensor. A water extract of each sample is prepared by punching out a circular filter segment (0.6 cm^2) containing the aerosol deposit. The segments are extracted in double distilled-deionized water.

Table 31. Chronology of the Washington University Car Travel

		End Points		Time		Time	Filter	Pass
Pass No.	Time	Start	End	LBL	Filter	2 MASS & β	Location	Label
October 19, 1976 - Experiment 1/293								
1	1444-1502	Background at Exposition Park				1444-1502	Expos. Pk.	
2	1500-1519	Exposition Ave to El Segundo		1502		1511		
3	1520-1532	El Segundo to Santa Monica						
4	1532-1536	Harbor & Santa Monica Junction to Western Ave						
5	1537-1540	Western Ave to Harbor Freeway						
6	1540-1543	Harbor & Santa Monia Junction to Exposition Ave			1548	1545	Expos. Pk.	
7	1548-1614	Background at Exposition Park				1548-1614	Expos. Pk.	
8	1712-1744	Background at Exposition Park		1712-1744		1712-1744		
October 20, 1976 - Experiment 2/294								
1	1419-1455	Background at Exposition Park				1419-1455	Bkgrd Site	Bkgrd
2	1544-1555	Vermont Ave to National Blvd		1536		1537		A to B
3	1556-1606	National Blvd to Vermont						B to A
4	1608-1618	Vermont Ave to National Blvd			1618	1618		A to B
5	1619-1638	National Blvd to Vermont Ave						B to A
6	1709-1730	Background at Exposition Park				1709-1730	Expos. Pk.	Bkgrd
(Assumed)								
7	1742-1750	Vermont Ave to National Blvd		1730		1730		A to B
8	1752-1800	National Blvd to Vermont Ave			1806	1806		B to A
9								
10								
11	1812-1835	Background at Exposition Park				1812-1835	Expos. Pk.	
October 21, 1976 - Experiment 3/295								
1	705- 749	Background at Rancho Park		705- 725 731- 749		705- 749	Rancho Pk.	Bkgrd
2	754- 810	Overland Ave to Vermont Ave		755		757		A to B
3	813- 823	Vermont Ave to National Blvd			823	823	Rancho Pk.	B to C
3a	831- 924	Background at Rancho Park		824- 914		831- 924	Rancho Pk.	Bkgrd
6	948- 956	Overland Ave to Vermont Ave		941		946		A to B
7	958-1006	Vermont Ave to National Blvd						B to C
8	1008-1016	National Blvd to Vermont Ave						C to B
9	1018-1026	Vermont Ave to National Blvd			1026	1026	Rancho Pk.	B to C
10	1047-1115	Background at Rancho Park				1047-1115	Rancho Pk.	Bkgrd

Table 31. Chronology of the Washington University Car Travel (Continued)

Pass No.	Time	End Points Start	End Points End	Time LBL Filter	Time 2 MASS & β	Filter Location	Pass Label
October 22, 1976 - Experiment 4/296							
1	650- 718	Background at Exposition Park		656- 719	700- 718	Expos. Pk.	
2	727- 738	Exposition Ave to El Segundo off Harbor		727	727	Expos. Pk.	
3	739- 800	El Segundo to Maple Ave					
4	800- 804	Maple Ave to Flower St		804	804	Expos. Pk.	
5	817- 904	Background at Exposition Park		824- 904	826- 904	Expos. Pk.	
6	912- 920	Exposition Park to El Segundo		912	915		
7	921- 938	El Segundo to Maple to Expos. Ave		939	939	Expos. Pk.	
8	958-1028	Background at Exposition Park			958-1028		
October 24, 1976 - Experiment 5/298							
1	1508-1537	Background at Rose Dale Cemetery		1508-1537	1510-1531	Rose Dale	
2	1537-1544	Enter Santa Monica to National Blvd		1537	1542		
3	1545-1554	National Blvd to Vermont Ave					
4	1556-1609	Vermont Ave to National Blvd		1613	1613	Rose Dale	
5	1627-1658	Background at Rose Dale Cemetery		1627-1658	1627-1658	Rose Dale	
6	1712-1724	Washington Ave, enter Harbor Freeway to El Segundo		1712	1712		
7	1724-1745	El Segundo to power failure		1745	1745		
October 25, 1976							
1	1540-1624	Background at VA Hospital		1553-1623	1553-1620	VA Hosp.	
2	1630-1637	Butler Blvd to LaTijera		1631	1635		
3	1639-1701	LaTijera to Mulholland Dr					
4	1705-1713	Mulholland Dr to Wilshire Blvd		1713	1713	VA Hosp.	
5	1728-1805	Background at VA Hospital		1728-1805	1729-1805		
6	1820-1830	Butler Blvd to LaTijera		1820	1820		
	1830-1850	LaTijera to Mulholland Dr					
	1850-1857	Mulholland Dr to Wilshire Blvd		1857	1857	VA Hosp.	
7	1913-1943	Background at VA Hospital		1913-1943	1913-1943	VA Hosp.	
8	1954-2033	VA Hospital to Caltech (Hill St.)		1958-2033	1958-2033		

Table 31. Chronology of the Washington University Car Travel (Continued)

Pass No.	Time	End Points Start End	Time LBL Filter	Time 2 MASS & β	Filter Location	Pass Label
October 26, 1976 - Experiment 7/300						
1	1327	Hill to Havenhurst		1327		A to B
2	1347	Havenhurst to Van Nuys Blvd		1347	S.O. Park	B to C
3	1409-1504	Background at Sherman Oaks Park	1409-1504	1416-1504	S.O. Park	Bkgrd
4	1516-1525	Van Nuys Blvd to Topanga Canyon Blvd	1516	1516		C to D
5	1529-1555	Topanga Canyon to Glenda Ave				E to F'
6	1556-1615	Glenda Ave to Van Nuys Blvd	1614	1614	S.O. Park	F'to C
7	1627-1722	Background at Sherman Oaks Park	1628-1722	1631-1722	S.O. Park	Bkgrd
8	1717-1742	Van Nuys Blvd to Topanga Canyon Blvd	1728	1733		C to D
9	1745-1825	Topanga Canyon Blvd to Hill Ave	1826	1826	Caltech	D to A
October 27, 1976 - Experiment 8/301A						
1	655- 722	Rosemead to Atlantic Blvd	722	706		A to B
2	724- 741	Atlantic Blvd to Citrus Ave				B to C'
3&4	743- 805	Citrus Ave to Rosemead	805	805	Rosemead	C'to A
5	813- 836	Background at Rosemead	813- 836		Rosemead	Bkgrd
6	841- 846	Rosemead to Atlantic Blvd	841	841		A to B
7	847- 901	Atlantic Blvd to Citrus				B to C'
8	904- 908	Citrus to Pacific	908	908	Pacific	C'to E
10	918-1057	Background at Del Norte Park	918- 950 1040-1-57	930-1057	Del Norte	Bkgrd
October 27, 1976 - Experiment 9/301B						
1	1350-1422	Hill Ave to Winnetka	1348	1347	Hill Ave	A to B'
2	1424-1433	Winnetka to Van Nuys Blvd	1433	1433	S.O. Park	B'to D
3						
4	1440-1643	Background at Sherman Oaks Park	1440-1643	1456-1643	S.O. Park	Bkgrd
5	1647-1649	Generator failure, lose LBL & thermograms				D to ?
6	1705-1715	East on Ventura; took wrong turn onto Hollywood Freeway		1706		
7	1720-1743	Off freeway into city traffic				
8	1727-1743	On Ventura to Hill Ave		1743	Hill Ave	
October 28, 1976 - Experiment 9/302						
1	1551-1800	Background at LACS Site	UM has our LBL	1618-1800	LACS	Bkgrd
2	1812-1854	LACS to Caltech		1824-1836	-	

Table 32. Summary of Sampling - Los Angeles Roadway Study

Date	Start Time LBL WU	Start Time LBL UM	End Time LBL WU	End Time LBL UM	Sampling	ΔT (min) WU Start	ΔT (min) UM End
10-20-76	1536	1543	1618	1614	Freeway	7	4
	1730	1740	1806	1815	Freeway	10	9
10-21-76	705	712	749	732	Background	7	17
	754	800	823	838	Freeway	6	15
	825		914		Background		
	941	945	1026	1023	Freeway	4	3
	1047	1045	1115	1115	Background	2	0
10-26-76		1336		1356	Freeway		
	1409	1411	1504	1456	Background	2	8
	1516	1509	1614	1609	Freeway	7	5
	1628	1623	1722	1708	Background	5	4
	1728	1742	1826	1826	Freeway	14	0
10-27-76	722	652	805	749	Freeway	30	16
	813		836		Background		
	841	828	908	921	Freeway	13	13
	918	945	950	1033	Background	27	17
	1040		1057				
	1348	1355	1433	1500	Freeway	7	27
	1440	1515	1643	1615	Background	35	32
		1640		1735	Freeway		
10-28-76		1616		1717	Background		
		1740		1842	Freeway		

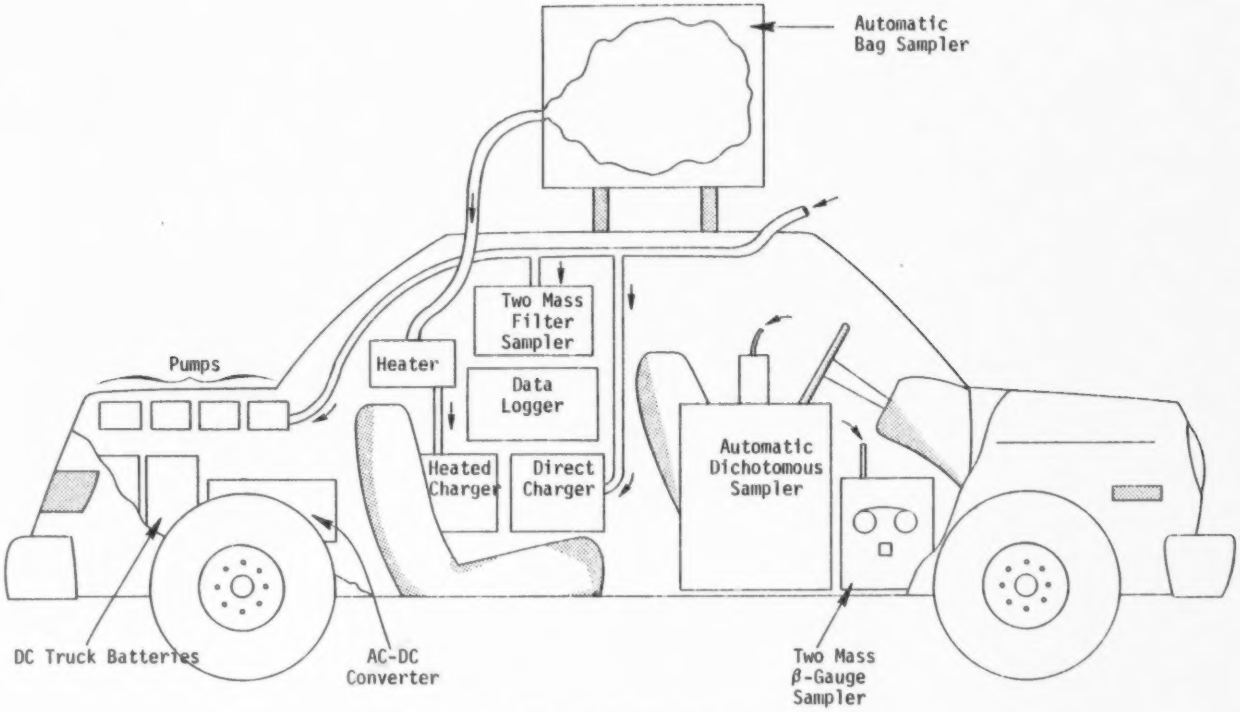

Automatic
Bag Sampler
Two Mass
Filter
Sampler
Heater
Pumps
Data
Logger
Heated
Charger
Direct
Charger
Automatic
Dichotomous
Sampler
DC Truck Batteries
AC-DC
Converter
Two Mass
β-Gauge
Sampler

Figure 16. Washington University Instrumented Car

The sulfur data from the TWOMASS sampler are given in Table 33. The net roadway sulfur values are calculated by taking the difference between the data obtained with two different samplers in two different vehicles. The mean of all these differences is -0.04 ug/m^3 S, and the standard deviation of the differences about the mean is 0.55 ug/m^3 S. The data do not include cases in which the Washington University car and the Caltech van were taking data side-by-side, so a direct determination of the possibility of sampling bias is not possible. However, it is possible to compare background and freeway data taken entirely by the sampler in the car, and this is done in Table 34. In this case, it is possible to say that a bias does exist because the background measurements are more often made earlier in the day than the freeway measurements, and the background aerosol sulfur concentrations tend to decrease during the day. Even so, a more elaborate data analysis would not be expected to change the conclusion that on the average, the net roadway sulfur concentration was within the experimental error of this data set.

One of the TWOMASS samplers was equipped to serve as a fully automated beta attenuation mass monitor. The mass of the fine particle fraction was determined by the absorption of ^{14}C beta particles in the sample. The mass results are given in Table 35. The accuracy of the aerosol mass concentrations with this instrument is 11%.

One of the aerosol chargers directly monitored the in-roadway aerosol concentration. The charger is an aerosol detector which responds primarily to aerosols in the 0.01 to 0.1 um size range (Husar, Macias, and Dannevik, 1976). The instrument operates on the principle of diffusion charging and subsequent detection by collection of the charged aerosol on a filter connected to an electrometer. The data from this instument were recorded every 0.5 sec on magnetic tape, and can be used for determining the commuter exposure to exhaust aerosol.

Figure 17 gives a schematic diagram of the thermal analysis system (Cobourn, Husar, and Husar, 1978) followed by the other aerosol charger. The thermal analysis measurement system consists of a continuous sampling system in which the aerosol flows first through a heat exchanger and then into the charger. The heat exchanger is a stainless steel tube which adds heat to the aerosol during the first 48 cm of travel through the tube, and then cools the aerosol down to ambient temperature during the remaining 218 cm of travel. The amount of heating is governed by a temperature contoller which can be programmed so that the exit aerosol temperature linearly increases from room temperature to 300 deg C. The rate of temperature increase can be adjusted from 20 deg C/min to 250 deg C/min. The heater exit

Table 33. Particulate Sulfate Data

Expressed as Concentration of Elemental Sulfur ($\mu g/m^3$)

Date	Time	Samples from WU Auto ($\mu g/m^3$)	B=Background F=Freeway	Time	Samples from Caltech Van (Background) ($\mu g/m^3$)	Net Roadway Sulfur ($\mu g/m^3$)
10-19-76	1444-1502	11.45	B			
	1511-1545	6.36	F	1507-1548	6.86	-0.50
	1548-1614	6.63	B	1548-1716	10.29	
	1712-1744	6.23	F	1716-1755	5.96	0.27
10-20-76	1419-1455	5.50	B			
	1537-1618	5.54	F	1536-1635	5.53	0.01
	1709-1730	4.26	B	1635-1726	5.43	
	1730-1806	3.81	F	1726-1845	2.99	0.93
10-21-76	747- 823	3.02	F	750- 829	2.29	0.73
	831- 924	2.27	B	829- 942	3.09	
	946-1026	3.06	F	942-1030	3.04	0.02
			B	1030-1045	3.27	
			B	1045-1115	3.16	
10-22-76	732- 804	2.92	F	717- 817	3.59	-0.67
	826- 904	2.37	B	817- 901	3.39	
	915- 939	3.35	F	901-1001	2.75	0.60
	958-1028	2.80	B	1012-1042	3.19	
10-24-76	1510-1531	2.73	B	1522-1552	4.02	
	1542-1613	2.86	F	1552-1658	3.27	-0.41
	1627-1658	3.11	B			
	1712-1745	3.06	F	1658-1738	2.70	0.36
10-25-76	1553-1620	2.75	B			
	1635-1713	3.22	F	1618-1715	4.13	-0.91
	1729-1805	3.07	B	1715-1800	4.05	
	1820-1857	2.89	F	1800-1854	3.61	-0.72
	1913-1943	2.43	B	1854-1907	3.33	
	1958-2033	1.82	F	1907-1935	3.29	-1.47
10-26-76	1327-1347	0.44	F			0.33
	1416-1504	0.11	B			
	1516-1614	0.25	F	1430-1612	0.90	-0.65
	1731-1722	0.11	B	1612-1625	0.92	
				1625-1712	0.18	
	1733-1826	0.33	F	1720-1810	0.17	0.16
10-27-76	706- 805	0.49	F	656- 757	0.44	0.05
	841- 908	0.66	F	757- 820	0.65	
	930-1057	0.28	B	904- 939	0.39	
				939-1032	0.67	
				1032-1037	6.59	

Table 33. Particulate Sulfate Data

Expressed as Concentration of Elemental Sulfur ($\mu g/m^3$) (Continued)

Date	Time	Samples from WU Auto ($\mu g/m^3$)	B=Background F=Freeway	Time	Samples from Caltech Van (Background) ($\mu g/m^3$)	Net Roadway Sulfur ($\mu g/m^3$)
10-27-76	1347-1435	0.43	F	1443-1507	0.69	-0.24
				1507-1511	0.46	
	1456-1643	0.29	B	1521-1622	0.26	
				1622-1641	0.19	
	1707-1743	0.67	F	1641-1726	0.23	0.44
10-28-76	1618-1800	0.57	B	1605-1655	0.70	
	1824-1836	0.46	F	1655-1734	0.74	
				1734-1819	0.82	
10-30-76				0313-0432	1.47	
				0432-0517	1.00	
				0517-0626	0.91	

Table 34. Average Daily Net Roadway Sulfur from the TWOMASS Sampler in the Washington University Car

Date	Average Freeway	Average Background	Difference F-B
	Aerosol Sulfur Concentrations $\mu g/m^3$		
19 October	6.30	9.04	-2.75
20 October	4.68	4.88	-0.21
21 October	3.04	2.27	0.77
22 October	3.14	2.59	0.55
24 October	2.96	2.92	0.04
25 October	2.64	2.75	-0.11
26 October	0.34	0.11	0.23
27 October AM	0.58	0.28	0.30
27 October PM	0.55	0.29	0.26
28 October	0.46	0.57	-0.11
		Mean	-0.10
		Standard Error	0.98

Table 35. Atmospheric Aerosol Mass Concentrations
Fine Particle Fraction
TWOMASS Beta Attenuation Mass Monitor

Date	Time	Sample	Location	MASS Conc. ($\mu g/m^3$)
10-24-76	1510-1531	Background	Rose Dale Cemetery	78.8
	1542-1613	Freeway	Santa Monica	107.9
	1627-1658	Background	Rose Dale Cemetery	99.8
10-25-76	1553-1620	Background	VA Hospital	59.5
	1635-1713	Freeway	San Diego	51.4
	1729-1805	Background	VA Hopital	32.8
	1820-1857	Freeway	San Diego	57.1
	1913-1943	Background	VA Hospital	17.8
	1958-2033	Freeway	San Diego-Ventura	56.3
10-26-76	1327-1347	Freeway	Ventura	43.2
	1416-1504	Background	Sherman Oaks Park	39.5
	1516-1614	Freeway	Ventura	32.6
	1631-1722	Background	Sherman Oaks Park	16.3
	1733-1826	Freeway	Ventura	21.1

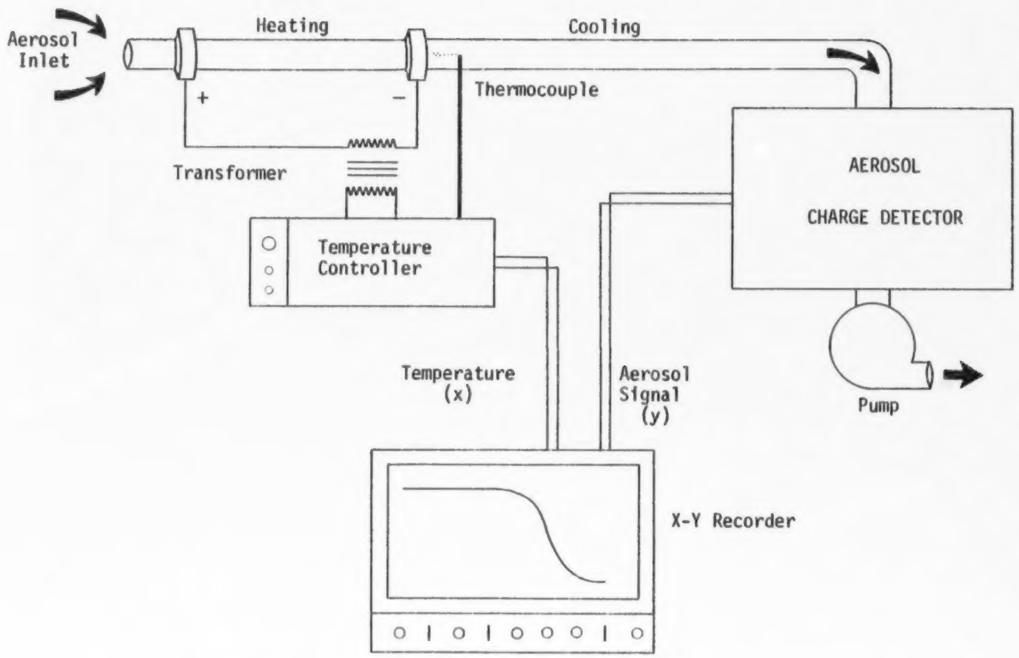

Aerosol Inlet
Heating
Cooling
+
−
Thermocouple
Transformer
Temperature Controller
AEROSOL CHARGE DETECTOR
Pump
Temperature (x)
Aerosol Signal (y)
X-Y Recorder

Figure 17. Diagram of the Thermal Analysis System

temperature and the aerosol signal are simultaneously recorded on an x-y recorder. Samples of data obtained with this system are shown in Figures 18 through 20. The first figure shows the response of the system to a calibration sulfuric acid aerosol. At a temperature between 100 deg and 200 deg C, the aerosol is vaporized in the heated tube and the vapors diffuse to the walls where they are adsorbed. The aerosol itself does not diffuse in this manner because its diffusion coefficient is many orders of magnitude smaller than that of the vapor. Each figure also contains an output record obtained when ammonia was added to the sample flow. When ammonia is added to the sample flow, ammonium sulfate is formed, and higher temperatures are required to volatilize this compound. The separation between the two curves is taken as being characteristic of sulfuric acid, and is used in ambient sampling to determine whether or not sulfuric acid is present.

Figure 19 shows a thermogram obtained on the Ventura Freeway. The inflections and change in separation of the two curves characteristic of sulfuric acid are not seen here, but it is interesting to note that ammonia has an appreciable effect on the aerosol volatility which extends down to rather low temperatures. After examining the charger data obtained from the field study, two general comments were made:

1. The charger signals on the roadway were in all cases at least 10 times the signals in the background sites;

2. There was a large residual charger signal at high temperature indicating the presence of some non-volatile roadway aerosol.

Figure 20 shows the only case in which sulfuric acid was clearly seen by the charger on the roadway. On this day, the experiment was conducted very early in the morning, so that traffic would be very light, and seven catalyst equipped cars were driven on the freeway ahead of the Washington University car and the University of Minnesota van. Therefore, these measurements were made under conditions in which sulfuric acid was expected to be present, and the concentrations of other particulates on the roadway were smaller than is typical on a congested freeway.

2.5 THE EPA DATA

A portion of the filter samples collected in the October field program were returned to T. G. Dzubay at Research Triangle Park for analysis by X-ray fluorescence (XRF). The data obtained for lead on filters exposed in the trichotomous sampler in the University of Minnesota van show clearly that

2-1

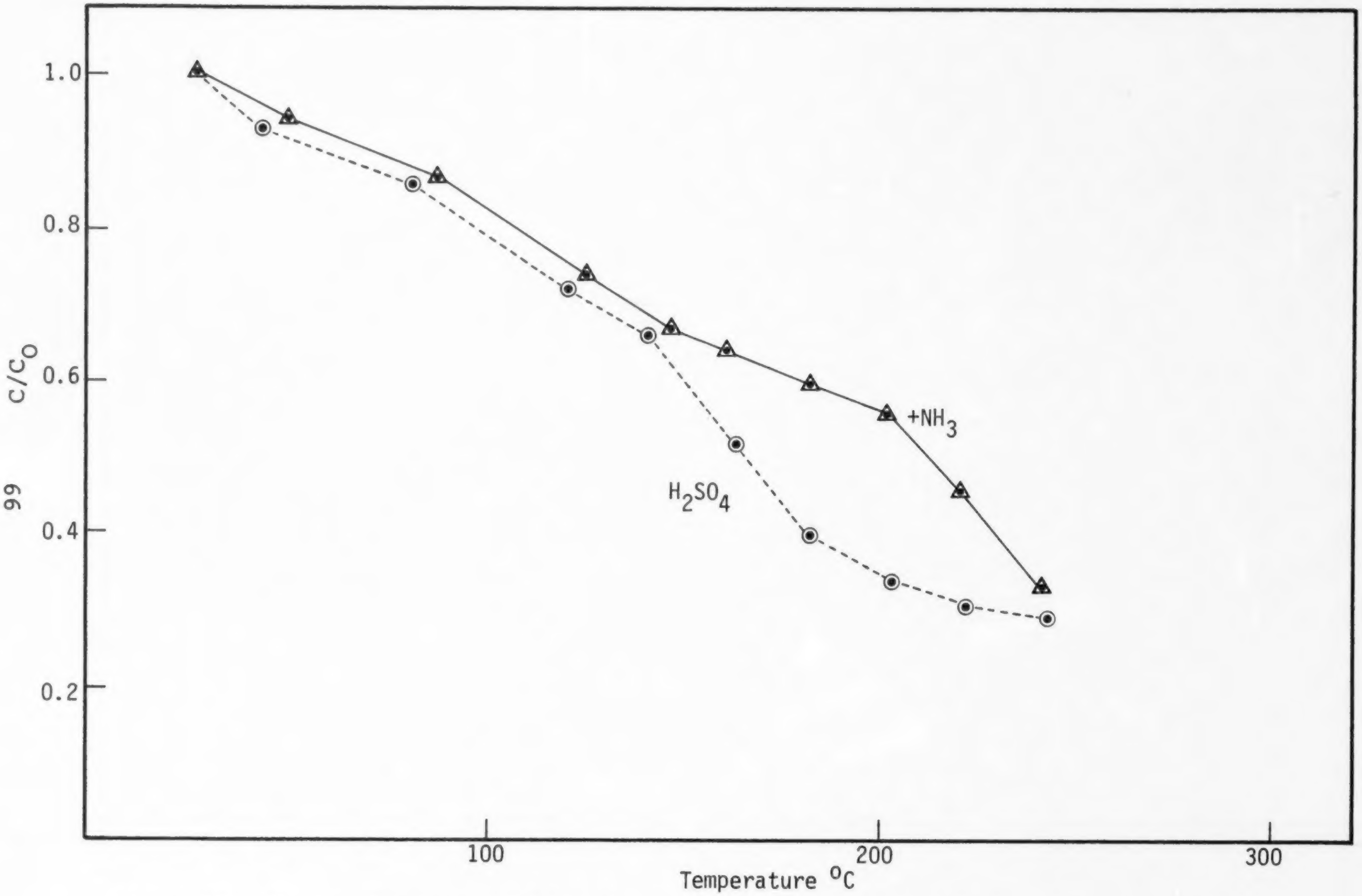


Figure 18. Charger Thermogram Calibration Using Sulfuric With and Without Ammonia Addition Performed at Caltech.

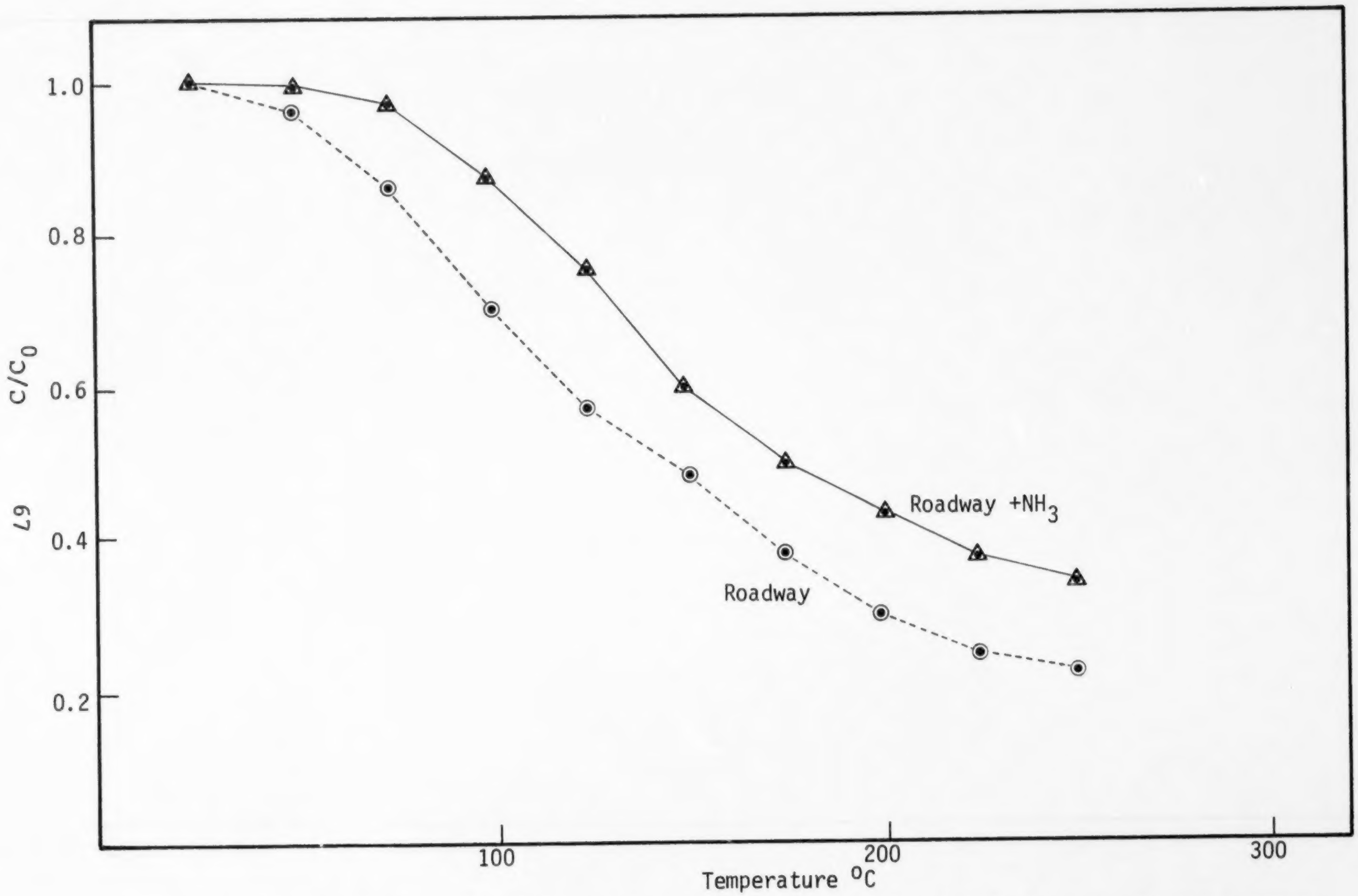


Figure 19. Charger Thermogram With and Without Ammonia Addition Obtained on the Ventura Freeway. (27 October 1977, 1352-1356 hr)

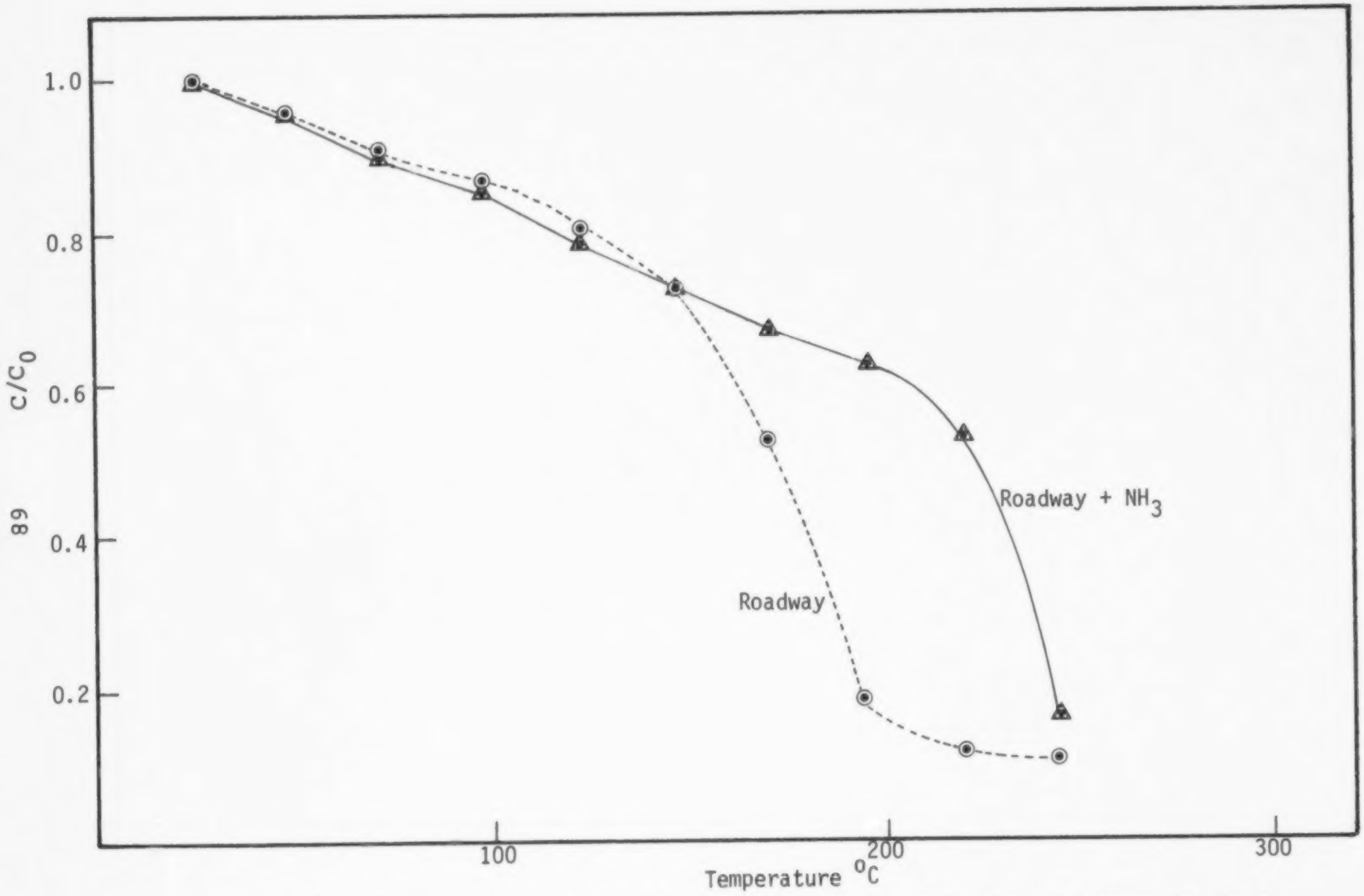


Figure 20. Charger Thermogram Showing Sulfuric Acid Obtained when Following Seven Catalyst-Equipped Cars. (30 October 1977)

large amounts of lead (more than 10 ug/m^3 in some cases) are present on the freeway in the nuclei mode size range. These data also provide a confirmation of the proper operation of the trichotomous sampler.

A journal article describing the lead and other chemical data obtained in this program has been prepared (Dzubay, Stevens, and Richards, 1979), and appears as Appendix B in this report. This article summarizes the more important data obtained from these XRF analyses.

2.6 THE ENVIRONMENTAL MONITORING AND SERVICES CENTER DATA

The main role of the Envrionmental Monitoring and Services Center (EMSC) in the field program was to provide analytical chemistry services for the rapid-turnaround analysis of filter samples. Over 400 wet chemical determinations were performed on 76 filters, and 71 filters were analyzed at Caltech by the Cabot Sulfuric Acid Monitor (SAM). The majority of these analytical results were reported during the course of the field program, and all of them were reported within a month of the end of the program. In addition, the EMSC obtained data for the background ammonia concentration, and provided logistical support in the form of ordering supplies and utilities, and delivering equipment.

2.6.1 Filter Chemistry Data

Aerosol samples were collected by various sampling devices in the three vehicles described in previous sections on 1 um Teflon filters, and then were returned to the laboratory at Caltech. There, the filters were placed in desiccators lined with glass filters coated with oxalic acid. The humidity in the desiccators was generally near ambient.

The filters were returned daily to the EMSC, where they were analyzed. The filters were cut from the supporting frames, ultrasonically extracted, and titrated for strong acid by the Gran procedure. Then the ammonium ion concentrations were determined by an ion selective electrode using a procedure in which standard additions of ammonium were made to avoid the problems with slow electrode response which occurs at very low concentrations. Finally, an ion chromatograph was used to analyze the extracts for sulfate, nitrate and bromide.

The complete tabulation of these data is not included here, but is available on request.

Table 36 summarizes the sulfate data taken with the LBL dichotomous samplers. It can be seen that as a general rule, there is no significant difference in the total small particle sulfate numbers on and off the freeway. This is true even on 26 October, when there were strong Santa Ana winds and the background sulfate concentration was about 0.5 ug/m^3. In contrast, bromide is clearly traffic related. The analysts in the laboratory could rather reliably identify filters collected on the freeway by their darker color and by their higher bromide content than those collected at background sites.

It is notable that no acidity was detected on the filters by the Gran titration. Before this result became known, a study to verify the ability to transport sulfuric acid from Caltech to the EMSC was initiated. Standard amounts of sulfuric acid aerosol, usually 9.8 ug per filter, were collected on a clean filter, and the filter was then put in among those returned from the field. Early in the first week of the study, it became apparent that even these filters produced no acidity in the Gran titration.

Therefore, an auxiliary experiment was planned. The sulfuric acid generator was transported to Thousand Oaks, and on Sunday, 24 October, aerosol samples were generated in the laboratory and the filters were extracted and titrated immediately. The recovery of the acid in these experiments was complete, as was the recovery of sulfate. Then the same apparatus and solutions were transported back to Pasadena and used without change, except that the nebulizer gas flow was obtained from a bottle of prepurified nitrogen. Again, without exception, the filters spiked with 9.8 ug of sulfuric acid showed no acidity when transported to Thousand Oaks and analyzed. The mean amount of sulfate on seven such filters was 9.72 ug, with a standard error of 1.1 ug. This corresponds to 9.9 ug sulfuric acid. Therefore, the sulfate was quantitatively transported on and extracted from the filters. To see if the prepurified nitrogen used to generate the aerosol might contribute to the problem, two of the above filter samples were generated using Scott-Marrin best quality zero air, with the same results.

In one experiment, 32.5 ug of sulfuric acid was deposited on the filter. In this case, acidity corresponding to 8 ug of sulfuric acid was found, and 29.9 ug sulfate (corresponding to 30.5 ug sulfuric acid) was found. Thus, some acidity was preserved when the larger amount of acid was used.

From these experiments, and the fact that ammonia denuders were not used during sampling, it is concluded that the measures used to preserve the sulfuric acid on the filters were not adequate, and that it is likely that any sulfuric acid collected

Table 36. Small Particle Sulfate Differences

Daily Averages of Data from the LBL Dichotomous Samplers

Date October 1976	Average Freeway Concentration $\mu g/m^3$	Average Background Concentration $\mu g/m^3$	Difference $\mu g/m^3$
19	13.16	13.19	-0.03
20	15.23	17.03	-1.80
21	6.71[a]	8.37	-1.66
21	8.77[b]	8.37	+0.40
22	8.21	7.50	+0.72
24	8.22	11.73	-3.51
25	8.81	11.97	-2.16
26[c]	0.40	0.67	-0.27
27[c]a.m.	1.50	1.02	+0.48
27[c]p.m.	0.98	0.71	+0.27

a. Average includes filter 202 with 0.5 $\mu g/m^3$ sulfate.

b. Average omits filter 202.

c. Only one freeway and on background sample analyzed.

on the freeway was lost before the analyses by the SAM, but no experiments were performed to confirm this supposition. Therefore, no definitive conclusion can be drawn from the small quantity of freeway related acidity or sulfuric acid observed in this field experiment. The impact of the catalysts is best estimated from the sulfate and aerosol sulfur data.

2.6.2 Ambient Ammonia Data

Shortly before the field program began, a request was received to measure ambient ammonia concentrations by the method which uses oxalic acid impregnated collection filters. The Environmental Monitoring and Services Center has performed a series of laboratory experiments to show that ammonia from a permeation tube could be quantitatively collected at a concentration of 5 ppb, extracted from the filter, and determined, but the method had not been used in the field. In this sampling method, ambient air was drawn through two filters at a rate of 7 l/min. The first was 1 um Fluoropore, to remove all ambient particulates, and the second was a Gelman A/E glass fiber filter impregnated with oxalic acid. In the ideal case, all ammonia gas in the sample is collected on the second filter as ammonium ion, and no ammonium containing particulates penetrate to the second filter.

The experimental procedure included the use of a field blank. The acid impregnated filters were taken to the field in one stack in one container. Two filters were removed from the middle of the pile for each experiment. One was placed in a petri dish, and the other was exposed to the ambient air flow and then placed in a similar petri dish. Both dishes were transported side-by-side to the laboratory for analysis in a plastic bag containing some oxalic acid coated paper. It was desired to collect samples at least in duplicate, but there was not time to prepare the necessary flow system. The data from the ammonia measurements are shown in Table 37. It should be noted that the ambient air contained enough ammonia to completely neutralize the sulfuric acid emitted on the freeways on all days included in this study.

2.6.3 Sulfuric Acid Monitor Data

An operator was provided for the Sulfuric Acid Monitor (SAM) built by the Cabot Corporation. The particular instrument used had been constructed just before the study, and required some field modifications, but it is believed that all essential portions of the instrument operated satisfactorily. The electronics of the SAM was intended to determine the area of the volatilization peak directly. However, the electronic method of subtracting the value of the zero sulfur signal was improper, so

Table 37.

Two-Filter Determinations of Ammonia Concentrations

Date October 1976	Sample Volume m^3	NH_4^+ Collected µg	NH_4^+ Blank µg	NH_3 Concentration µg/m^3
24	0.71[a]	1.28	0.06	2[a]
25	1.08	8.68	0.08	8
26	1.05	2.89	?	3
27	0.93	6.00	0.22	6
28	0.80	2.38	- 0.08	3
30	1.46	1.77	0.04	1

a. The flow rate, hence the volume sampled and the concentration, are uncertain on 24 October.

the data were read from a stripchart record of the linearized FPD output using a planimeter to integrate the area under each volatilization peak.

The SAM was calibrated with sulfuric acid droplets rather than aerosols because better reproducibility was obtained. A summary of all calibration data is contained in Table 38. It can be seen that the response from a given amount of sulfuric acid was rather variable. Because the calibration data did not appear to have a trend during the course of the sampling program, it was decided to use one calibration curve for all data. This was established by plotting the data as in Figure 21, where the mean and the range of signals for each amount of acid are shown. Then the calibration curve was drawn by eye through the data. The dashed line indicates the nominal calibration of the Cabot SAM.

The best SAM data were obtained from the LBL dichotomous samplers, but these filters were submitted to the SAM only early in the program. A summary of the results is presented in Table 39. It can be seen that the SAM signals are generally larger on the freeway than at the background site, and that this is especially true on 21 October. The total SAM signals were also largest on this day.

The next best SAM data were obtained from filter B of the trichotomous sampler, which contains the same aerosol cut size range as the small particle samples from the LBL samplers. The filter B data are less good than those from the LBL samplers primarily because the sampling flow rate, and hence the sample size, is smaller. The data are summarized in Table 40. On the average, the freeway signals are larger than those obtained for the background sites, but the difference is not statistically significant.

The presence of large background signals usually made it difficult to observe sulfuric acid on the freeways using the SAM. However, on Tuesday 26 October, the Santa Ana winds blew the smog out of the basin and reduced the sulfate concentrations to about 0.5 ug/m^3. On that day, the SAM signals were appreciably larger on the freeway than at the background sites, but the difference between the apparent concentrations of sulfuric acid was only 0.07 ug/m^3. As mentioned previously, it should be kept in mind when interpreting these data that the measures taken to preserve the sulfuric acid after collection and before analysis probably were not adequate.

One significant finding in the data from the SAM is that all samples collected on days when smog was present showed signals like those from sulfuric acid, and the apparent sulfuric acid concentrations were as large as 1.2 ug/m^3. These signals were also observed in the Caltech parking lot, and had been

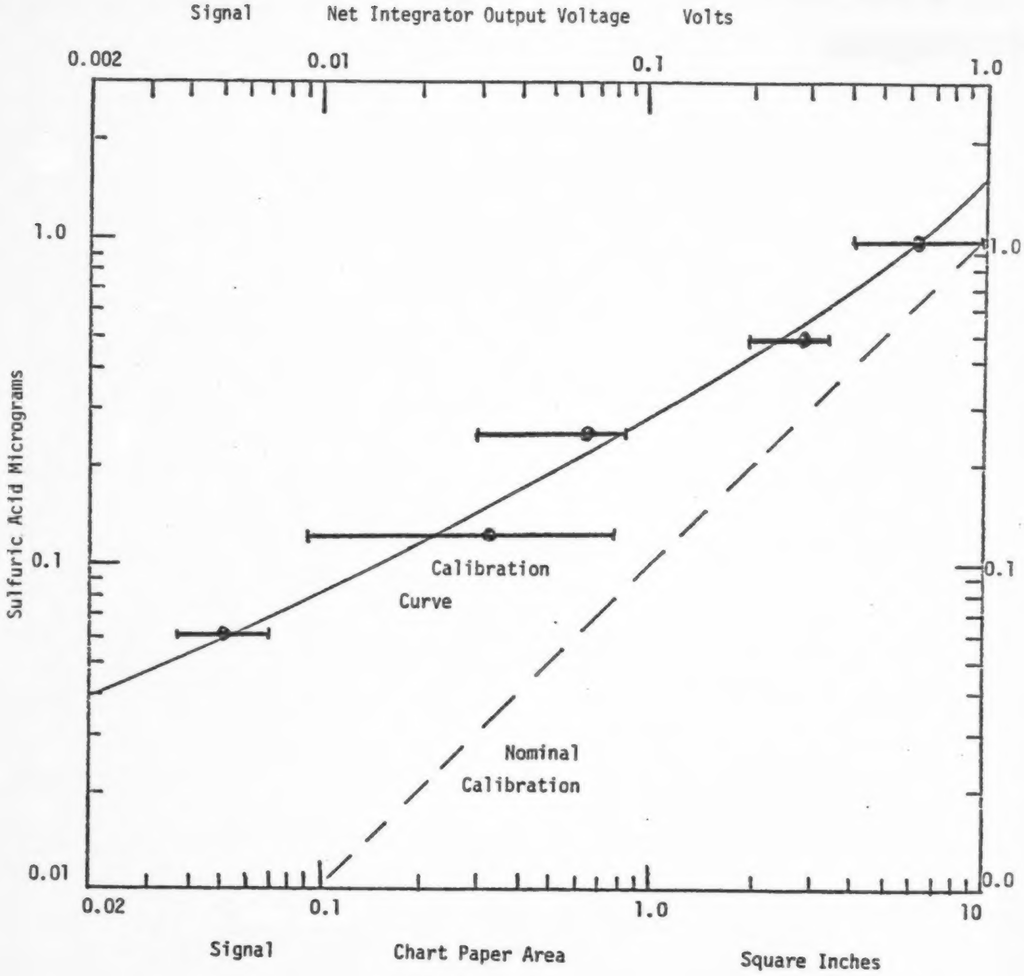


Figure 21. Sulfuric Acid Droplet Calibration of the SAM

Table 38. Sulfuric Acid Monitor Calibration Data

(2.5 μl droplets)

Acid Concentration N	Weight H_2SO_4 μg	No. of Calibrations	High Signal Volts	Low Signal Volts	Mean Signal Volts	Std. Dev. Volts
0.008	0.98	17	1.0	0.39	0.63	0.20
0.004	0.49	4	0.34	0.19	0.29	0.07
0.002	1/4	14	0.089	0.025	0.063	0.022
0.001	1/8	11	0.078	0.009	0.032	0.026
0.0005	1/16	5	0.006	0.004	0.0051	0.0014

Table 39. Sulfuric Acid Monitor Data from the LBL Sampler Filters, Freeway and Background Data Grouped by Day

Date October 1976	Site[a]	No. of Data Points	Mean $\mu g/m^3$	Std. Dev. $\mu g/m^3$	Difference[b] F-B $\mu g/m^3$
20	F	2	0.80		-0.14
20	B	1	0.94		
21	F	3	1.24	0.03	0.33
21	B	3	0.91	0.12	
22	F	2	0.77		0.21
22	B	2	0.56		
24	F	2	0.51		0.06
24	B	1	0.45		

a. F = freeway B = background

b. Mean daily difference = 0.12 $\mu g/m^3$

Table 40. Sulfuric Acid Monitor Data from the Trichotomous Sampler B Filter

Date October 1976	Site F = freeway B = background	SAM Reading µg/m^3	Difference F-B µg/m^2
25	F	0.75	0.15
	B	0.60	
26	F	0.22	0.07
	B	0.15	
27 am	F	0.15	-0.18
	B	0.33	
27 pm	F	0.24	0.05
	B	0.19	
28	F	0.48	0.31
	B	0.17	
30	F	0.12[a]	-0.07
	B	0.19	
mean			0.14

[a] The instrument attempted to relite the flame (which was on) at the start of this measurement.

observed several months earlier in experiments conducted by the EMSC in Thousand Oaks.

Because sulfuric acid concentrations were not expected to be this large away from the freeways, two experiments were performed in which duplicate samples were collected in the Caltech parking lot. One filter was analyzed directly, and the other was exposed to the vapors from a concentrated ammonia solution before analysis. Since the volatilization conditions were such that ammonium sulfate and ammonium bisulfate would not give a signal, any sulfuric acid on the filter should no longer give a signal after the ammonia treatment. The results of the experiments are given in Table 41. It can be seen that about 40% of the original signal appears to be due to some volatile, sulfur containing compound other than sulfuric acid. These experiments repeat similar ones performed earlier at the Environmental Monitoring and Services Center in Thousand Oaks, California, in which an average of one-third of the signal persisted after ammonia treatment in 15 duplicate filter samples.

To learn more about the substance which causes this response, the ratio of the SAM reading to the wet chemical sulfate determination was calculated for the 20 cases in which both quantities were determined for the same filter. A summary of these ratios, expressed as a percentage, is presented in Table 42. It can be seen that the ratio varied from 4% to 17%, and that the average ratio is 10%. This average has essentially the same value on and off the freeway. Thus, if the SAM response were entirely due to sulfuric acid, an average of about 10% of the sulfate observed in this field experiment was sulfuric acid. The data summarized in Table 42 are presented another way in Figure 22, where a scatter diagram shows that the SAM reading does not correlate with the total sulfate reading.

The nature of the substance giving this response of the SAM is not known at this time. One speculation which might partially explain these observations is that the aerosol in the South Coast Air Basin might contain some volatilizable organic sulfur compounds. It is also possible that a portion of the observed signal is due to sulfuric acid.

Table 41.

Sulfuric Acid Monitor Data from Samples
Collected 20 October in the Caltech Parking Lot

Sample Time	Sample Volume m^3	Ammonia Exposure	SAMM Signal Volts	Apparent H_2SO_4 per Filter μg	Apparent H_2SO_4 Concentration $\mu g/m^3$
09:00 - 09:30	1.4	no	0.93	1.4	1.0
09:00 - 09:30	1.0	yes	0.16	0.39	0.4
09:30 - 10:00	1.4	no	1.1	1.65	1.2
09:30 - 10:00	1.0	yes	0.2	0.45	0.45

NOTE: Both samples not exposed to ammonia were collected with the LBL dichotomous sampler in the University of Minnesota van, and both samples exposed to ammonia were collected in the LBL sampler in the Washington University car.

Table 42. Sulfuric Acid Monitor (SAM) Readings
Divided by Total Sulfate Expressed as Percent

			$\frac{\text{SAM}}{\text{Sulfate}} \times 100$			
Sampler[(a)]	Location[(b)]	No. of Samples	Minimum	Maximum	Mean	Standard Deviation About Mean
LBL & TSV-B	B & F	13	4	16	9.8	4.2
LBL & TSV-B	B	4	4	13	9.5	4.0
LBL & TSV-B	F	9	4	16	9.9	4.5
LBL & TSV	B & F	20	4	17	10.4	3.9

Notes:

(a) LBL = Fine fraction from the LBL samplers in the car and in the van

TSV-B = Filter B from the Trichotomous sampler in the van

TSV = Filters B, C and D from the Trichotomous sampler

(b) B = Background site

F = On the Freeway

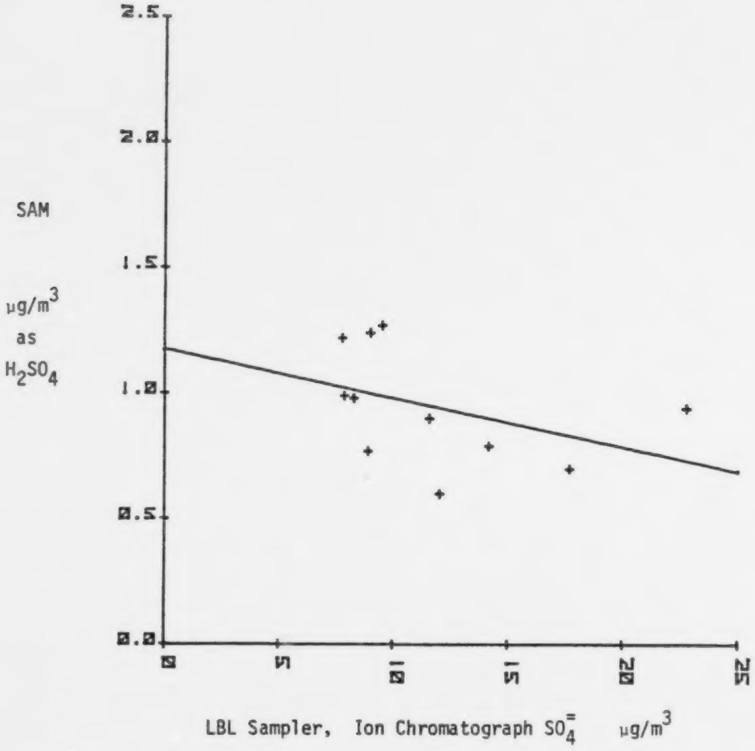


Figure 22. Correlation of the SAM Reading with the Sulfate Concentration Determined from the Same Filter

3.0 INTERPRETATION OF THE 1976 DATA

To provide a background for the data interpretation, this section begins by modifying earlier estimates of the sulfate concentrations on roadways so that the population of catalyst equipped vehicles and the emission rates are in accord with the most recent data. Then the measurement methods used in the October field program are compared with each other, and finally, the combined results are used to place upper limits on the in-roadway sulfate concentrations present during this study.

3.1 ESTIMATES OF THE CATALYST VEHICLE POPULATION

Two methods have been used to estimate the population of catalyst equipped vehicles on the Los Angeles roadways in October, and they both give the result that between 25% and 30% of the light-duty vehicles were catalyst equipped.

One of the methods was a count of vehicles conducted by an observer in the University of Minnesota van. The results are given in Table 30 and the counting methods are described in the accompanying text. The range of values was 18% to 33% catalyst equipped automobiles, and the mean of the daily values gives the result that 29% of the automobiles on the freeways had catalysts.

The second method of estimating the fraction of catalyst equipped vehicles is based on registration data and mileage distribution data. Information from the California Division of Motor Vehicles was used to estimate that in late October, the fraction of automobiles in Los Angeles equipped with catalysts was 13.5% (Parry, Meyer, and Rodes, 1977). In making these estimates, care was taken to properly account for new foreign cars, such as the Honda, which do not have catalysts.

The vehicle registration data must be combined with estimates for the number of miles traveled by each age of vehicle to obtain values for the vehicle mix on the roadway. Table 43, from a report by TRW (1976) to the California Air Resources Board (CARB), gives vehicle population and mileage data appropriate for 1975. The estimates are based on unpublished data supplied by the CARB staff to TRW. The vehicle number distribution estimates were derived by examining registration and scrappage rate information, and were presented in terms of vehicle age instead of model year. The conversion to model year was made by TRW. The estimated annual mileage for

Table 43. Vehicle Population and Mileage Distribution by Model Year (from TRW, 1976)

Light Duty Passenger			
Model Year	Number Distribution	Mileage Distribution	VMT Distribution
1975	0.00380	16350	0.00778
1974	0.06470	15190	0.12305
1973	0.09860	13650	0.16851
1972	0.09700	12000	0.14573
1971	0.09450	10450	0.12364
1970	0.09200	9060	0.10436
1969	0.08750	7770	0.08512
1968	0.08200	6610	0.06786
1967	0.07450	5570	0.05195
1966	0.06650	4650	0.03871
1965	0.05650	3860	0.02730
1964	0.04600	3189	0.01837
1963	0.03450	2640	0.01140
1962	0.02550	2220	0.00709
1961	0.01850	2000	0.00463
1060	0.01400	2000	0.00351
1959	0.01050	2000	0.00263
1958	0.00790	2000	0.00198
1957	0.00600	2000	0.00158
1956	0.00400	2000	0.00100
1955	0.00300	2000	0.00075
1954	0.00250	2000	0.00063
1953	0.00250	2000	0.00063
1952	0.00250	2000	0.00063
1951	0.00250	2000	0.00063
Pre-1951	0.00250	2000	0.00063
TOTAL	1.00000		1.00002*
AVG		7987	

*Small error due to rounding

each model year is based on data accumulated during an emissions test program conducted by the CARB. As the emissions tests were being conducted, the odometer reading of each vehicle was recorded. The mileage charts were then analyzed, and a series of estimates of mileage based on vehicle age were developed. These estimates were then converted to the corresponding model years for use in the model of the inventory. The data show that the newest vehicles drive about twice as far per vehicle per year as the population as a whole. Therefore, the estimate that 13.6% of the automobiles are equipped with catalysts leads to the estimate that they account for 27% of the miles traveled by automobiles. This result is in excellent agreement with the vehicle counts obtained from the University of Minnesota van.

3.2 SULFATE EMISSION RATE DATA

One of the first findings that emerged from the early work to determine the rate of emission of sulfates from catalyst equipped automobiles was the variability of the emission rate. This variability is an important characteristic of the data, and cannot be neglected in any assessment of the catalyst sulfate problem. In particular, it should be noted in the data below that the variability in the sulfate emission rate is probably as important as the variability in the atmospheric dispersion conditions.

Perhaps the most useful sulfate emission rate data for the present program are those recently obtained at Olson Laboratories under an EPA contract (Herling, Gafford, Carlson, Lyles, and Bradow, 1977). A summary of the sulfate emission rate data obtained in this study is given in Table 44. The mean emission rates are low compared to previous data. The grand mean was 13.6 mg/mi (8.5 mg/km), the mean from the HFET (highway test) was 16 mg/mi (9.9 mg/km), and the mean of the four S-7 tests on the vehicles at 12,500 miles was 7.5 mg/mi (4.7 mg/km). These numbers are to be compared with the 37 mg/mi (23 mg/km) observed for new California cars in the General Motors Sulfate Dispersion Experiment. The Olson data have been criticized by Pierson (1977) because the emission rates are smaller than would be expected on the basis of data taken in other laboratories, and furthermore because the Olson Laboratories data give smaller sulfate emission rates than do other laboratories in the EPA Baseline Experiment (Somers, Garbe, Lawrence, and Baines, 1977). However, his criticism leaves open the possibility that consumer-owned vehicles have significantly lower sulfate emission rates than do the test vehicles. Recent data by Pierson, Brachaczek, and McKee (1979) have shown that the sulfate emissions of catalyst equipped cars in tunnels on the Pennsylvania Turnpike are best estimated as 12 ± 4 mg/mi (8 ± 3 mg/km).

Table 44. Sulfate Emission Rate Data for Approximately 100
Consumer-Owned Vehicles in California (Herling, 1977)

Summary of Fleet SO_4 Emissions (mg/mi)

Driving Cycle	Test Series 1 (n = 101)				Test Series 2 (n = 94[1])				Test Series 3 (n = 92)			
	Min.	Max.	Mean	σ	Min.	Max.	Mean	σ	Min.	Max.	Mean	σ
FTP	0.1	37.0	4.3	7.3	0.1	66.8	2.9	7.4	0.2	15.2	2.0	2.6
1st S-7	0.1	134.3	17.1	25.4	0.1	58.7	10.1	12.7	0.2	45.7	5.9	6.8
2nd S-7	0.1	80.2	15.6	20.9	0.1	71.0	9.9	14.3	0.1	48.8	6.5	8.9
HFET	0.1	115.6	22.3	27.5	0.1	86.6	15.8	20.5	0.3	57.0	9.8	11.8
3rd S-7	0.1	108.8	16.0	21.0	0.1	92.2	10.9	16.2	0.2	58.0	8.0	12.3
4th S-7	0.1	118.5	16.7	22.7	0.1	68.7	11.7	16.8	0.2	67.0	9.0	14.0

[1] For FTP, Test Series 2, n = 95.

Average Vehicle Mileage at Test Time

Test 1	3,500
2	8,000
3	12,500

Some support for this possibility can be found in the data collected by the New York State Department of Environmental Conservation (Gibbs, Wotzak, Byer, Johnson, Hill, and Werner, 1977). They tested a sample of forty-nine 1975 and 1976 catalyst equipped vehicles at 5,000 mi (8,000 km) intervals and found average sulfate emissions of 4.1 mg/mi (2.5 mg/km) in a one-hour 50 mph (80 kph) cruise, and 2.7 mg/mi (1.7 mg/km) in the S-7 (congested freeway) test. However, these cars were not equipped to meet the California emission standards.

It is also important to note in the Olson Labs data that some emission rates are very high. At 3,500 miles, the maximum emission rates were above 100 mg/mi (62 mg/km), and the 95% confidence limit on the emission rate was about 50 mg/mi (31 mg/km). Therefore, some vehicles produce high local concentrations of sulfate on the roadways. Recent SF_6 tracer experiments by F. H. Shair and co-workers at Caltech have determined dilution factors in the plumes behind vehicles on freeways. Part of their results can be summarized by the equation,

$$x/Q = 0.179 \exp(-L/213 \text{ ft}) \text{ ug m-3 mi mg-1}$$

for distances L between the emitting vehicle and the measuring vehicle up to 400 ft (122 m), and no intervening vehicles (Palmer and Shair, 1977). This equation indicates that emission rates Q of 100 mg/mi (62 mg/km) can lead to concentrations x of 10 ug/m^3 at the location of following vehicles. (One hundred mg/mi is 62 ug/m, so dispersing the exhaust uniformly over a 2 m x 3 m = 6 m^2 area would lead to a concentration of 10 ug/m^3.) Should two or three vehicles with high emission rates drive near each other for a time, it is possible to generate sulfate exposures for the following vehicles which are high enough to be of concern. For example, three vehicles emitting 100 mg/mi could produce local concentrations in the 30 ug/m^3 range.

Most previous estimates of the sulfate exposures which might be experienced on freeways have focused on the high concentrations produced by conditions of extreme stagnation, when the emissions from many vehicles (perhaps thousands) are combined in a small volume of air. For these estimates, the average emission rates should be used, and the latest data show that in general these rates are low. Therefore, it now appears that these episodes will not be as severe as indicated by the early estimates. A more quantitative discussion of this point is given in Section 3.4.

3.3 BACKGROUND CONCENTRATIONS DUE TO VEHICULAR SULFATE EMISSIONS

The background levels of sulfate produced by catalyst equipped vehicles are of interest for two reasons. First, sulfate levels in an urban area are of concern because of the resultant visibility reduction and the possibility that sulfates are associated with adverse health effects. Secondly, a measurement program to determine the impact of sulfate emissions due to vehicles cannot make measurements in true background locations which are free of those emissions. It is only possible to make measurements a few blocks away from major streets and roadways, where there are no important sources in the immediate vicinity. Therefore, it is of interest to estimate the general sulfate levels which might be produced in the Los Angeles area by catalyst equipped vehicles.

An estimate of this kind has been made by Cass (1975), so the desired information can be obtained by revising his calculations to be in accord with present estimates of the vehicle population and emission rates. Estimates were constructed by Cass for the cases listed in Table 45. The results for cases IA and IB are shown in Figures 23 and 24.

In the sulfate emission study carried out by Olson Labs to determine the sulfate emission rates of consumer-owned vehicles in the Los Angeles area (Herling, Gafford, Carlson, Lyles, and

Table 45. Summary of Assumptions for Sulfate Air Quality Computations

Case	Fraction of Gasoline-Powered Vehicle Miles Traveled with Oxidation Catalysts	Approximate Number of Model Years Involved	Approximate Year	Sulfur Content of Gasoline	$SO_4^=$ Emission Factors (gm/mile) Urban Cycle	$SO_4^=$ Emission Factors (gm/mile) Highway Test	Traffic Growth Multiplier Applied to 1969 Traffic Counts
IA	50.7%	3	1978	0.026%	0.013	0.042	9 yr @ +2%/yr = 1.195
IB	50.7%	3	1978	0.026%	0.013	0.042	9 yr @ +4%/yr = 1.423

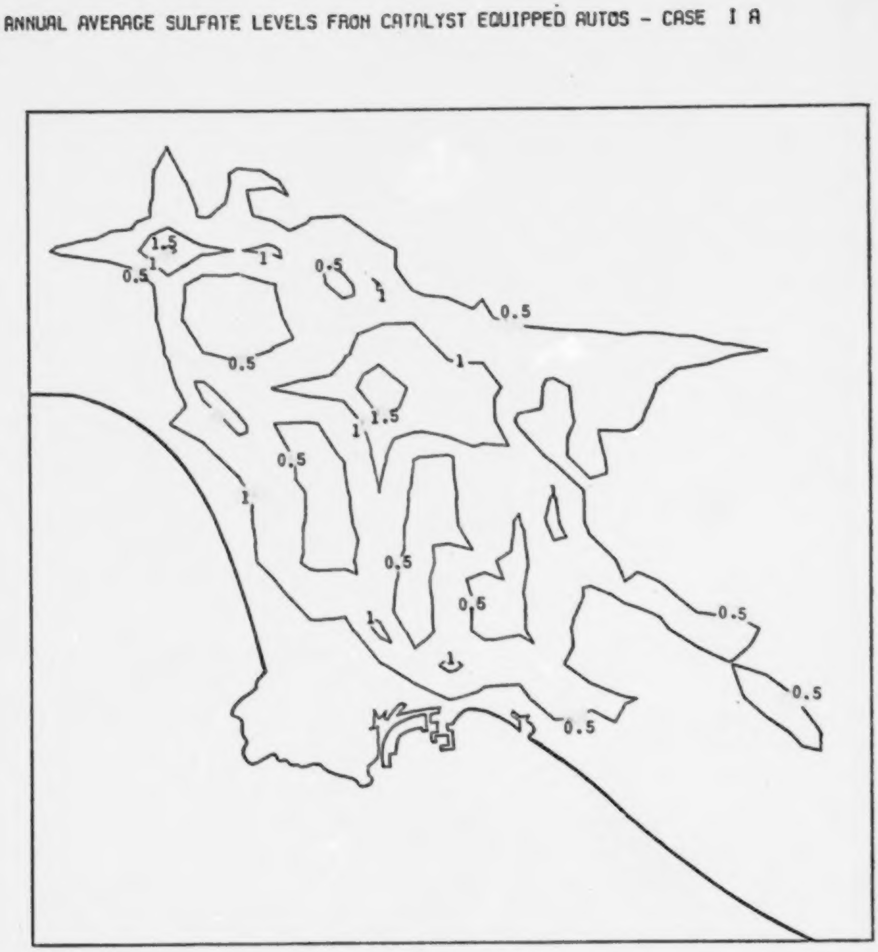
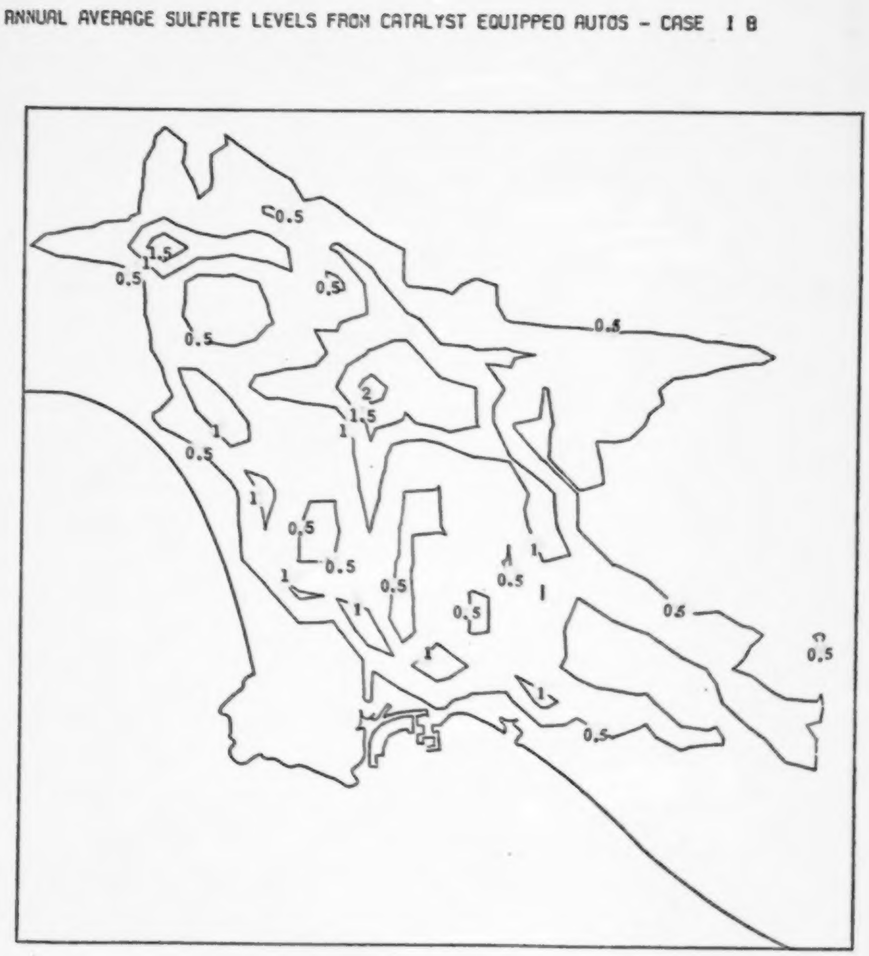

ANNUAL AVERAGE SULFATE LEVELS FROM CATALYST EQUIPPED AUTOS - CASE I A
1.5
1
0.5
1
0.5
1
0.5
0.5
1
1.5
1
0.5
1
0.5
0.5
1
1
0.5
0.5
0.5

Figure 23. Projected Annual Average Sulfate Levels from Catalyst Equipped Autos - Case IA. All Values in $\mu gm/m^3$ as H_2SO_4. See Table 4-3 for List of Assumptions. (Cass, 1975).



ANNUAL AVERAGE SULFATE LEVELS FROM CATALYST EQUIPPED AUTOS - CASE I B

0.5
1.5
1
0.5
0.5
0.5
0.5
2
1.5
1
1
0.5
1
0.5
0.5
1
1
0.5
1
0.5
1
0.5
0.5
1
0.5
1
0.5
0.5

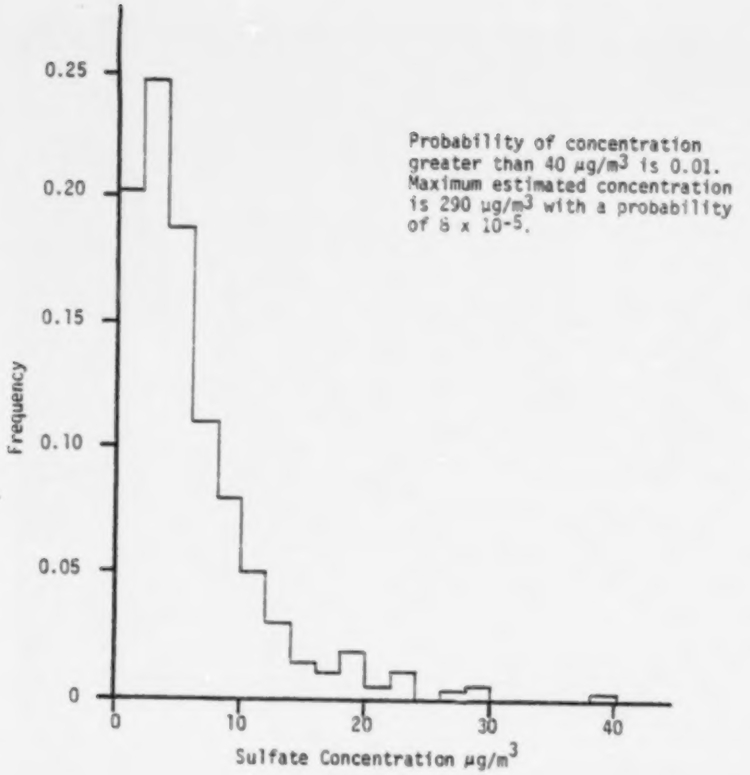
Figure 24. Projected Annual Average Sulfate Levels from Catalyst Equipped Autos - Case IB. All values in μgm/m^3 as H_2SO_4. See Table 4-3 for List of Assumptions. (Cass, 1975).

Bradow, 1977), the sulfur content of the fuel in the vehicles when they were brought in by the owners was measured, and an average of 0.027% S was found. However, as shown in Table 44 and discussed above, the sulfate emission rates observed in this study were low. Average values obtained from the Table are 3.1 mg/mi (1.9 mg/km) in the FTP (urban cycle) test and 16 mg/mi (9.9 mg/km) in the HFET (highway) test. Using the fact that about 60% of the vehicle miles in Los Angeles are on surface streets and 40% on freeways (Cass, 1975), the emission rates reported by Herling et al. are one-third those used by Cass. Also, the fraction of the vehicle miles traveled by catalyst equipped vehicles in October is estimated to be between 25% and 30%, instead of 50%, and the sulfate emission rate dropped rapidly with increasing mileage in the vehicles tested by Herling et al. Therefore, if the Olson data are correct, the concentrations in Figures 23 and 24 should be divided by at least a factor of five. The result is that estimates of the background concentrations are near 0.1 ug/m^3 for most of Los Angeles, and they rise to approximately 0.3 ug/m^3 in the downtown area.

The finding in the Olson Labs study that the sulfate emission rates decrease rapidly with vehicle age indicates that a steady state emission rate may be approached well before the time the vehicle population approaches 100% catalyst cars. If this is the case, the background sulfate concentrations in Los Angeles due to primary sulfate emissions from vehicles may remain below 0.5 ug/m^3.

3.4 ESTIMATES OF ROADWAY SULFATE CONCENTRATIONS

The existence of previous estimates of sulfate concentrations to be expected on the Los Angeles freeways permits scaling these estimates to obtain data that should apply to late 1976. In this report, the data of Papetti and Horowitz (1975) shown in Figure 25, will be used as the starting point. They were taken from an internal EPA paper, which appears as Appendix A in this Report. The approach taken in that paper is to combine data for actual commuter trips taken is Los Angeles, sulfate emission rates, and the range of meteorological conditions which occur over a one year period in Los Angeles and to use the EPA HIWAY model to obtain estimates of the distribution function which describes the frequency of occurrence of various in-roadway sulfate concentrations due to catalyst equipped vehicles. An important conclusion obtained from this work was that the highest sulfate concentrations are expected to occur with a vanishingly small probability, and the sulfate concentrations from catalyst equipped vehicles which are to be expected most of the time are not large enough to be of great concern. The data derived in this report were intended to be an upper bound, and hence were based on the assumption that



Probability of concentration greater than 40 $\mu g/m^3$ is 0.01. Maximum estimated concentration is 290 $\mu g/m^3$ with a probability of 8×10^{-5}.

Figure 25.

Frequency Distribution of Emitted Sulfate Concentrations on a Freeway With 17,000 Catalyst Equipped Vehicles Per Hour. These Concentrations Are One-Half Those Predicted by the HIWAY Model Using the Distribution of Hourly Meteorological Conditions at the L. A. International Airport Between 6 and 9 a.m. in 1964 and a Sulfate Emission Rate of 35 mg/mi.
(Papetti and Horowitz, 1975).

the traffic density remained constant at 17,000 catalyst equipped vehicles per hour. However, the meteorological inputs to the HIWAY model were selected so as to represent the distribution of conditions that might occur in a typical year.

One of the findings of the General Motors Sulfate Dispersion Experiment was that the HIWAY model tends to overpredict the roadway concentrations when the wind speed is below 0.5 m/sec, and that the overpredictions can be as large as a factor of 16 (Chock, 1976, 1977). In part, this is due to the turbulence generated by the vehicles and the plume rise resulting from the heating of the air on the highway, which play an important role in the dispersion process under stagnant conditions, but are not accounted for in the HIWAY model. Therefore, it appears likely that the data in Figure 25 overestimate the probability of the very high concentrations. In the following discussion, no attempt is made to correct for this.

To scale the data in Figure 25 to the present conditions, the emission rate should be reduced from 35 mg/mi (22 mg/km) to roughly 14 mg/mi (8.7 mg/km) if the data of Herling, et al. (1977) are correct, and the fraction of catalyst automobiles should be set between 25 and 30%. Thus, the sulfate concentrations should be divided by approximately a factor of ten, if no corrections are made to the HIWAY model beyond those already included in Figure 25. This means that in the fall of 1976, a freeway with a traffic density of 17,000 vehicles per hour would have concentrations of sulfates from catalyst vehicles that were below 0.5 ug/m^3 most of the time, and concentrations that reach 29 ug/m^3 with a probability of 8 x 10^{-5}, and the latter number is an overestimate for the reasons given above. These numbers, calculated from average emission rates, are not large compared to those calculated from roadway sulfate concentrations produced by the few vehicles in the population which have high emission rates. Therefore, sampling programs designed to determine the frequency of expsoure to high sulfate concentrations should be able to observe the high concentrations produced by a few vehicles with unusually high emission rates as well as high concentrations which occur when the wind speed is unusually low.

The frequency distribution of emission rates for new catalyst equipped vehicles is not available at this time, but it is interesting to assume that the data in Table 44 form a representative sample. Then one out of 100 catalyst vehicles with a mileage below 4000 emits 100 mg/mi (62 mg/km), and that one out of 200 emits more than 50 mg/mi (31 mg/km). If the average vehicle travels 100,000 miles, these vehicles will constitute 4% of the population. If only these vehicles are considered, the probability of a vehicle emitting 100 mg/mi is 4 x 10^{-4} and the probability of a vehicle emitting 50 mg/mi or more is 2×10^{-3}. Some vehicles with greater than 4000 miles emit more than 50 mg/mi, so the total fraction of vehicles with a emission rate greater than 50 mg/mi might be 1×10^{-2}. Then the probability of finding two of these vehicles together is similar to that of finding one vehicle which emits 100 mg/mi.

These probabilities are not well enough known to justify pursuing these estimates further, but it can be seen that the probability of finding high sulfate concentrations on the roadway caused by a few cars with high emission rates are similar to those of finding high sulfate concentrations due to poor dispersion conditions.

When examining the data from the October field program, it should be remembered that the vehicles which took the data made a point of driving a few miles an hour more slowly than the general traffic, so that the unusual concentrations produced by the unusual vehicles would not cause wide fluctuations in the data from the filter samples. Therefore, this source of variation in the data was averaged out in approximately the same way as it would be by a fixed monitoring site. In future freeway sampling, consideration should be given to moving with the traffic in such a way that the true variability in the exposure of the population appears in the experimental data.

3.5 COMPARISON OF THE AEROSOL SULFUR MEASUREMENT METHODS

The primary technique used in this section to compare different measurement methods is the scatter diagram and a linear least squares fit to the data, shown by a solid line. When appropriate, the diagrams also include a dashed line to show the locus of points representing a perfect agreement between the methods. Because the objective of the study is to detect a small increment of sulfate in the roadway, and this requires taking the difference between measurements made on and off the roadway, it is important to examine the experimental methods carefully to determine what biases, however small, exist in them. Therefore, the comparisons in this section have been made.

Figure 26 shows a comparison of the TWOMASS sampler data for total aerosol sulfur with the ion chromatograph sulfate data for all cases in which a direct comparison can be made. Only cases in which the two samplers are operated side-by-side in the same vehicle are included in this Figure. The average agreement between the methods is good, but there is significant scatter.

Figure 27 shows a comparison between data taken by the Caltech Low Pressure Impactor (LPI) in two different vehicles when the vehicles were operated side-by-side at the background site. These data clearly show a bias, and it appears that the

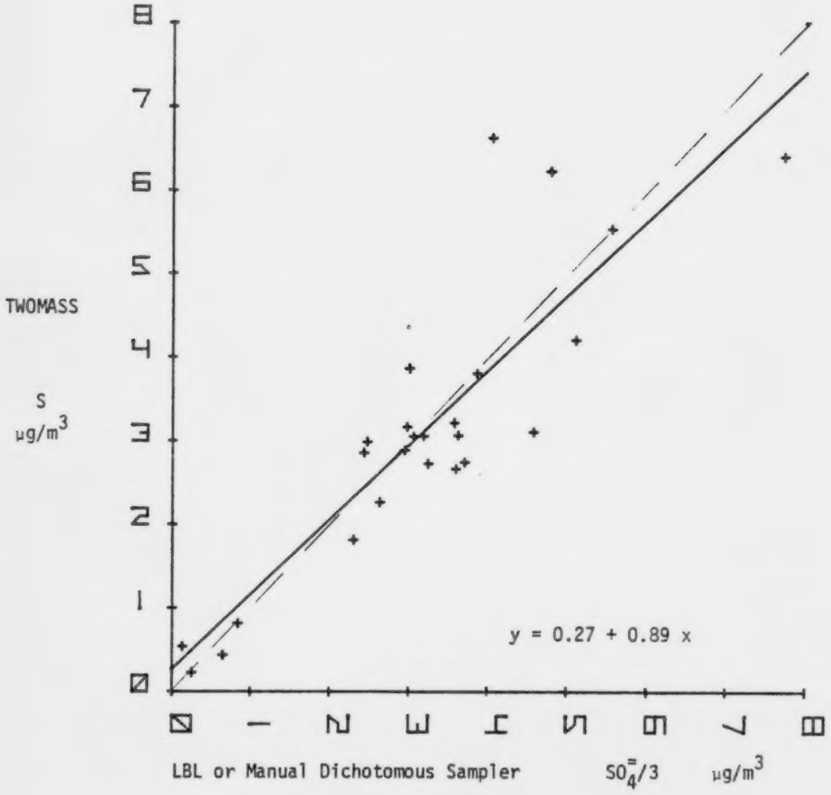


Figure 26. Scatter diagram comparing data from the TWOMASS and virtual dichotomous samplers. Both samples in the Caltech van or in the Washington University car.

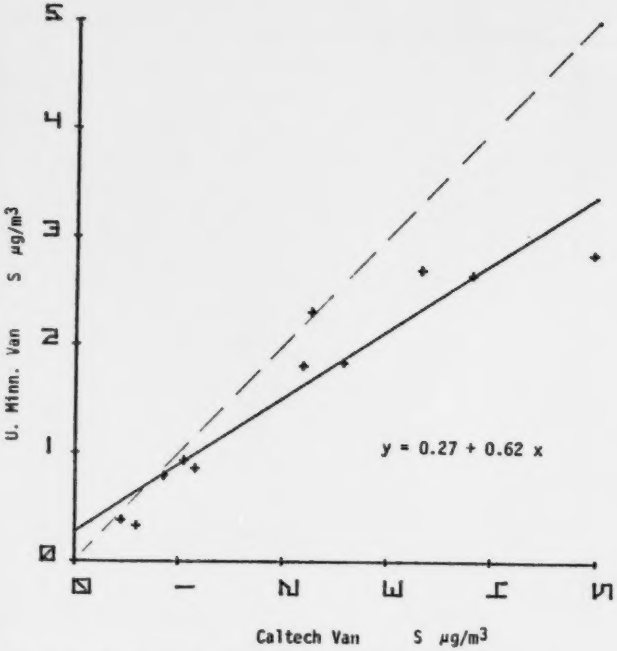


Figure 27. Scatter diagram comparing sulfur data from two LPI's in different vehicles at the background site.

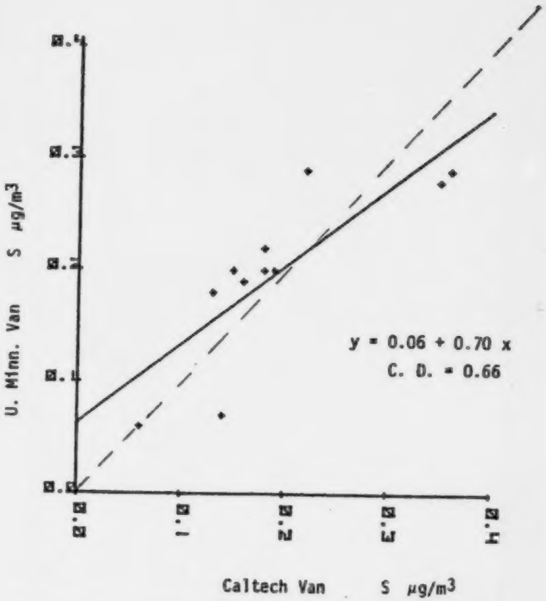


Figure 28. Scatter diagram comparing small particle (< 0.12 µm) sulfur data from two LPI's in different vehicles at the background site.

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sampling system in the University of Minnesota van is less efficient than the sampling system in the Caltech van. Figure 28 shows data from the same runs, except that only sulfur collected on the last two impactor stages was considered. Here the data scatter about the equal response line (dashed) in such a way as to indicate that the two sampling systems had equal efficiency for particles smaller than 0.075 um.

The LPI total sulfur data and ion chromatograph sulfate data taken in the Caltech van at the background site are compared in Figure 29. These results suggest a sampling and collection efficiency for the LPI that is less than unity. The same comparison for data obtained in the University of Minnesota van is shown in Figure 30. Here the scatter in the data is small, but the discrepancy between the two measurement methods is even more pronounced.

Figure 31 shows a comparison between data from the TWOMASS sampler and the LPI in the Caltech van. The lower efficiency of the LPI is in agreement with the data presented earlier. These two samplers were in different vehicles for the in-roadway sampling, so a comparison between results in that environment must be preceeded by a demonstration that data from the two vehicles are comparable when similar measurement methods are used. This appears in Figure 32, where data from the LBL dichotomous samplers as determined by the ion chromatograph are compared. There are fewer data points than would be desirable for a comparison of this kind, but the reasonable agreement found there permits the comparison in Figure 33, where the in-roadway and background data from the LPI in the University of Minnesota van are compared with the TWOMASS sampler data in the Washington University car. In agreement with the results presented above, the LPI in the University of Minnesota van gives significantly smaller results.

The final comparison, in Figure 34, relates the sulfate concentrations determined with the ion chromatograph from filters collected by two different samplers in the University of Minnesota van. In both cases, the air flow is processed by a dichotomous sampler and the fine particle fraction is collected. These data suggest that the losses in the trichotomous sampler are greater.

In general, it can be said that the agreement between the various aerosol sulfur measurement methods is good, and when there is a bias between methods, the scatter in the data about the regression line is reasonably small. However, when the in-roadway increments of sulfate are being estimated from these data, care must be taken to account for the biases which do exist in these results.

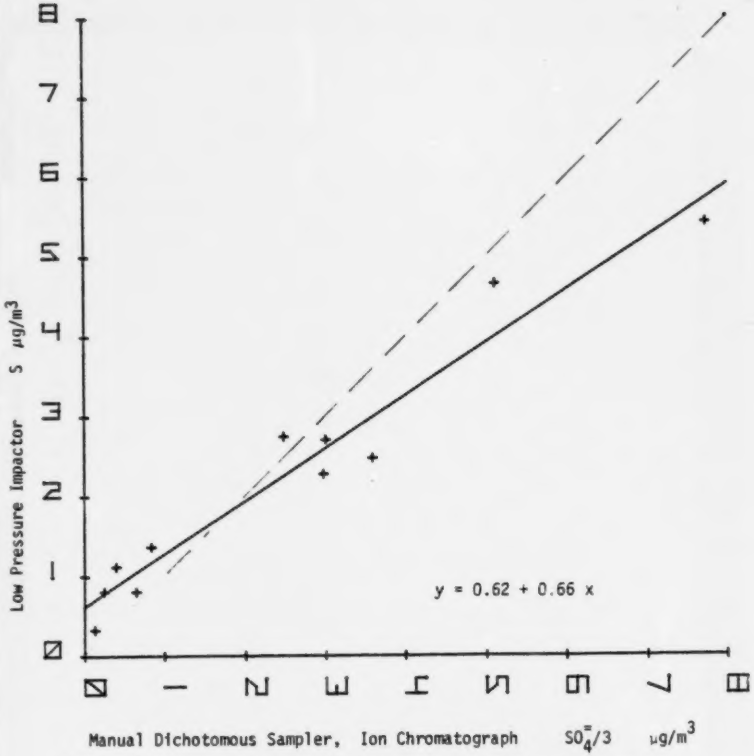

Figure 29. Scatter diagram comparing LPI data with dichotomous sampler data in the Caltech van at the background site.

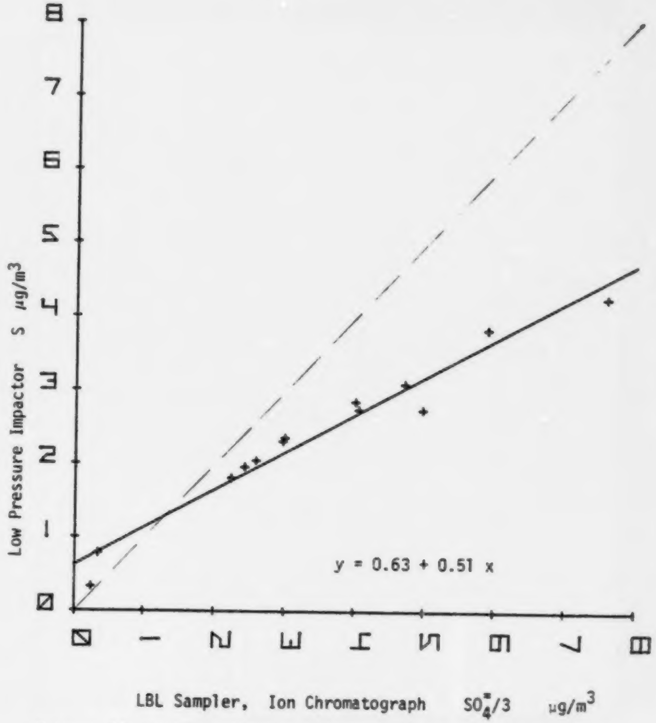

Figure 30. Scatter diagram comparing LPI data with dichotomous sampler data in the University of Minnesota van.

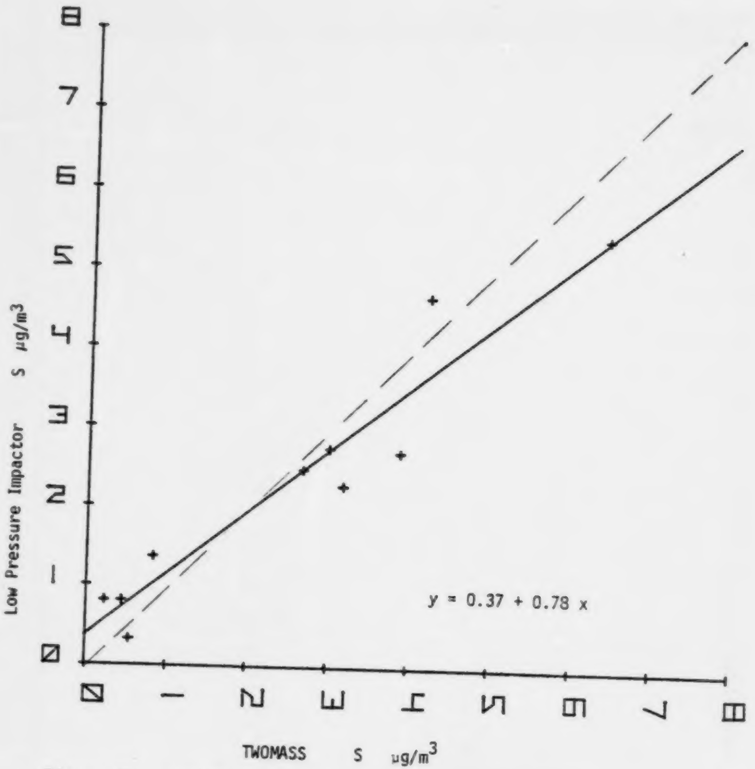

Figure 31. Scatter diagram comparing LPI data with TWOMASS sampler data in the Caltech van at the background site.

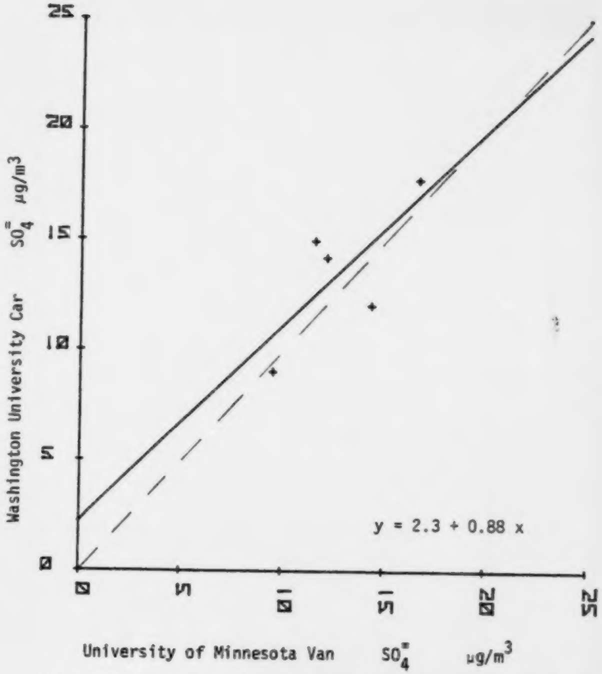

Figure 32. Scatter diagram comparing ion chromatograph sulfate data obtained with the LBL dichotomous sampler in the Washington University Car and the University of Minnesota Van.

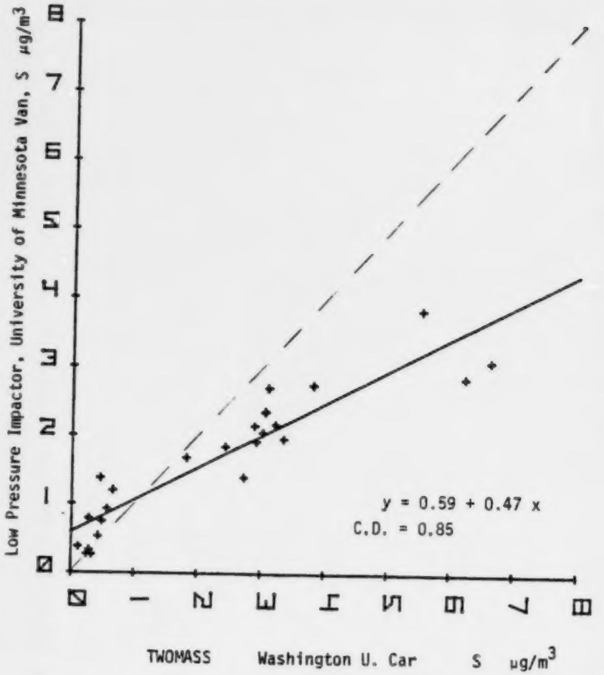

Figure 33. Scatter diagram comparing sulfur data obtained with the LPI in the University of Minnesota Van and the TWOMASS sampler in the Washington University Car.

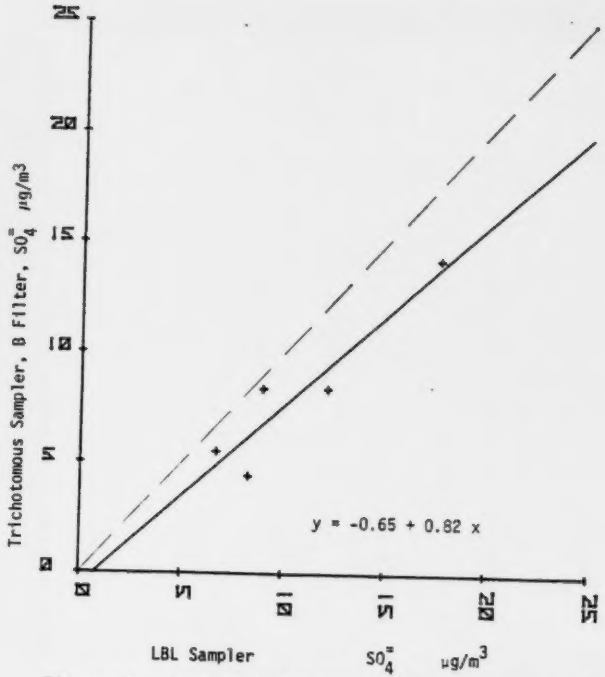

Figure 34. Scatter diagram comparing ion chromatograph sulfate data obtained with the trichotomous sampler and the LBL dichotomous sampler in the University of Minnesota Van.

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3.6 ESTIMATES OF THE ROADWAY SULFATE INCREMENT ON 21-26 OCTOBER

The following general statements can be made about the data for sulfur compounds obtained in the October field program:

1. All measurement methods detected increased concentrations of sulfuric acid or sulfates on the roadway at some times during the program;

2. On the average, the increments in the roadway sulfate concentrations were within the experimental error;

3. At no time did all measurement methods simultaneously detect an increment in the roadway sulfur compounds. However, most of the measurement methods detected a sulfuric acid or sulfate increment on 21 October.

The difficulty in detecting increments in the sulfate concentrations on the roadway due to catalyst equipped automobiles arises primarily from the background aerosol concentration. In general, at this time of year, sulfate levels in Los Angeles are near or above 10 ug/m^3, and the concentration of this background sulfate is rather variable in both time and in space. In the 1976 field program, the background measurements were usually significantly separated in both time and location from the in-roadway measurements, and this is believed to have been the major cause of the variability in the observed values for the increments in the in-roadway sulfate concentrations. The in-roadway sulfate data from this field program are of special interest on two days. The first is October 21, when the following observations were made:

1. The highest readings from the Cabot sulfuric acid monitor (SAM) were obtained on this day, as well as the largest increment on the roadway;

2. October 21 and 27 are the only days in which all values obtained during the day for the net roadway sulfur by the TWOMASS sampler were positive;

3. The sulfate data from the LBL dichotomous samplers gave a positive reading. This occurred in the daily average data from four out of nine experiments.

A summary of the sulfate or sulfur data obtained on this day are given in Table 46. As shown in Section 3.5, the low pressure impactor (LPI) data in the University of Minnesota van are known to be biased, so the negative value for the UM-CIT difference arises from causes that have been identified. The only other negative value in the table also comes from the LPI, but the roadway sulfate increment determined by this method is positive on most other days (see the left hand data column of Table 4).

Table 46. Freeway-Background Sulfate Differences

Observed on 21 October 1976

Collection Method	Analytical Method	Daily Average		Difference F-B	Units	Sulfate Difference $\mu g/m^3$
		Freeway	Background			
LBL Dichot.	SAM	1.24	0.91	0.33	$\mu g/m^3$ H_2SO_4	0.3
TWOMASS (WU)	FV-FPD	3.04	2.27	0.77	$\mu g/m^3$ S	2.3
TWOMASS (WU-CIT)	FV-FPD	3.04	2.67	0.38	$\mu g/m^3$ S	1.1
LBL Dichot.	Ion Chrom.	8.77	8.37	0.40	$\mu g/m^3$ $SO_4^=$	0.4
LPI (UM)[a]	FV-FPD	2.20	2.31	-0.10	$\mu g/m^3$ S	-0.3
LPI (UM-CIT)[a]	FV-FPD	2.20	2.48	-0.28	$\mu g/m^3$ S	-0.9
LPI (UM)[b]	FV-FPD	0.29	0.16	0.13	$\mu g/m^3$ S	0.4
LPI (UM-CIT)[b]	FV-FPD	0.29	0.20	0.09	$\mu g/m^3$ S	0.3
					Mean[c]	0.6
					Standard Deviation[c]	0.8

a. All stages of the low pressure impactor. The UM readings are known to be too small.

b. Stages 7 and 8, which nominally collect particles 0.02 to 0.12 μm in diameter.

c. The value -0.9 is excluded.

The mean value of the sulfate increments (excluding the value known to be biased) is 0.6 ug/m^3. The traffic volume during this experiment was 10,000 cars per hour (see Table 8).

October 26 is of special interest because the Santa Ana winds began on this day, with the result that the visibility became excellent and the background sulfate values dropped below 1 ug/m^3. From the comparison of the data in Table 22 with those for other days, and the comparison between Tables 28 and 29, it can be seen that the Santa Ana winds did not appreciably reduce the in-roadway concentrations of the automotive emissions. Therefore, 26 October should be an ideal day to see the sulfates from catalyst equipped automobiles. In fact, the experimental data scatter about zero, as shown in Table 47. This is the day on which the Cabot SAM saw roadway signals that were much larger than the background signals. However, the signals were small, less than 0.3 ug sulfuric acid per filter, because the volume of air sampled was small.

The measured background ammonia concentration on this day was 3 ug/m^3, which is capable of neutralizing more than 8 ug/m^3 of sulfuric acid. No traffic data are available for the Ventura Freeway on this day.

3.7 AN ESTIMATE OF IN-ROADWAY SULFATE INCREMENT ON 30 OCTOBER

Very early in the morning on 30 October 1976, an experiment was performed in which the Washington University car and the University of Minnesota van followed seven other catalyst equipped automobiles. The timing was chosen so that the other traffic on the freeway was very light. The chronology of the run and other experimental conditions are given in Table 19 and Figure 7.

The experimental results are given in Table 26 and Figures 13, 14, and 20, as well as in other general tabulations of data. The Washington University thermal speciation device and charger clearly saw sulfuric acid (Figure 20). Also, it is interesting that the aerosol difference distribution in Figure 14 shows that the emitted aerosol was essentially all in the nuclei mode size range. This agrees with the results of the General Motors Sulfate Dispersion Experiment (Whitby, et al., 1976; Wilson, et al., 1977), and contrasts sharply with all of the other data obtained in this program, which were obtained with the vehicle mix normally present of Los Angeles freeways. The typical vehicle mix also contributes accumulation mode aerosol to the in-roadway atmosphere.

The data in Figure 14 give a value of 6.4 um^3/cm^3 for the increase above background of the volume of nuclei mode aerosol. The data in Table 26 show that the average temperature was 11.3

Table 47. Freeway-Background Sulfate Differences

Observed on 26 October 1976

Collection Method	Analytical Method	Daily Average Freeway	Daily Average Background	Difference F-B	Units	Sulfate Difference g/m^3
Trichot. B	SAM	0.22	0.15	0.07	µg/m^3 H_2SO_4	0.07
TWOMASS (WU)	FV-FPD	0.34	0.11	0.23	µg/m^3 S	0.7
TWOMASS (WU-CIT)	FV-FPD	0.29	0.53	-0.24	µg/m^3 S	-0.8
LBL Dichot.	Ion Chrom.	0.40	0.67	-0.27	µg/m^3 $SO_4^=$	-0.27
LPI (UM)[a]	FV-FPD	0.27	0.38	-0.11	µg/m^3 S	-0.33
LPI (UM-CIT)[a]	FV-FPD	0.27	0.26	+0.01	µg/m^3 S	0.03
LPI (UM)[b]	FV-FPD	0.10	0.06	0.04	µg/m^3 S	0.1
LPI (UM-CIT)[b]	FV-FPD	0.10	0.05	0.06	µg/m^3 S	0.2
					Mean	-0.04
					Standard Deviation	0.4

a. All stages of the low pressure impactor. The UM readings are known to be too small.

b. Stages 7 and 8, which nominally collect particles 0.02 to 0.12 µm in diameter.

deg C, and the average relative humidity was 62%. Under these conditions, the aerosol sulfuric acid has a weight concentration of 37% (Gmitro and Vermeulen, 1964), and a specific gravity of 1.28. If all of the nuclei mode aerosol were sulfuric acid of this composition, the concentration of pure sulfuric acid would be 3.0 ug/m^3.

These data can be converted into an estimate of the sulfuric acid emission rate of the catalyst equipped automobiles by using the sulfur hexafluoride data of Palmer and Shair discussed in Section 5.2. If it is assumed that only the vehicles in the lane ahead of the University of Minnesota van contributed to the in-roadway concentrations observed by the van, that all four vehicles had the same sulfuric acid emission rate, that the vehicle spacing was 50 ft (15 m), and that the given equation is also approximately correct when there are intervening vehicles, then the emission rate for the four vehicles is calculated to be 7.3 mg/mi or 4.5 mg/km. This number is smaller than would be expected on the basis of the Olson Labs data for consumer-owned vehicles (Herling, et al., 1977), but is in a reasonable range. It is significantly smaller than the 35 mg/mi (22 mg/km) observed in the General Motors Sulfate Dispersion Experiment.

3.8 COMMENTS ON LOS ANGELES IN-ROADWAY SULFATE INCREMENTS IN OCTOBER 1976

The above results, and those for the other days which appear in Section 2.0, show that the sulfate concentrations on roadways due to catalyst equipped automobiles are small enough in comparison with the background sulfate concentrations that they are obscured by the scatter in the data on all of the October, 1976 days in which experiments were conducted. It is believed that most of the scatter in the data for in-roadway increments of sulfate arise from the variability of the background sulfate concentrations, and the appreciable separation in time and space of the in-roadway and background measurements. On a clean day with good ventilation and a low sulfate background, the sulfate increase due to catalysts was still not clearly seen, and was almost certainly below 1 ug/m^3. These findings are in agreement with the predictions of low sulfate concentrations based on atmospheric dispersion models and sulfate emission rates presented in Section 3.4.

It is not possible, on the basis of only the data obtained in this two-week field experiment, to give an upper limit for the sulfate concentrations on Los Angeles freeways. Because most of the data for the in-roadway sulfate increments are within the experimental error, it is even difficult to give an upper limit to the in-roadway sulfate increments sampled by the van and the car. Based on a subjective review of the data, it is estimated that if the in-roadway sulfate increment had been in the neighborhood of 2 ug/m^3 during a number of the filter averaging times, the increment would have been clearly seen in the data. Therefore, it is believed that the actual in-roadway sulfate increments during the filter sampling times in this program were nearly always smaller than 2 ug/m^3.

It should be pointed out that the physical aerosol measurements show large contributions of the roadway to the background aerosol concentration on all days. Therefore, the sulfate emissions from catalyst equipped vehicles are a small part of the total aerosol emissions on roadways at this time.

3.9 CORRELATIONS AMONG OTHER DATA MEASURED IN THE UNIVERSITY OF MINNESOTA VAN

This section contains a series of scatter diagrams showing the relation between the in-roadway concentrations of several of the measured gases and aerosol components. The points show the data in Tables 21 and 22 for times when the the van was operating on the freeway. The background data usually show little enough variability that the range of values is within the size of the symbol B on the diagram, which indicates the average background concentrations. When the background concentrations showed more variability, bars are used to indicate the observed range of the data. In most diagrams, the NOx concentration is the dependent variable. NOx was singled out in these comparisons because its concentrations on the roadway were well above the background, it is easily measured, and the NOx concentration is not affected by the reaction of the emitted NO with the ambient ozone.

Figure 35 shows an excellent correlation between NO and NOx on both days. Figure 36 shows that NO_2 correlates with NOx rather well. Some of the observed NO_2 is directly emitted, some is formed from the reaction of the emitted NO with the ambient ozone. The calculations for taking account of the reaction with ambient ozone can be easily carried out (Peters and Richards, 1977), and the analysis of the data for 21 October gave the result that 5% or 6% of the NOx emitted by vehicles is in the form of NO_2 as it enters the atmosphere.

Some correlation between SO_2 and NOx is shown in Figure 37 but the correlation between the CO and NOx concentrations in Figure 38 is very poor. The lack of correlation in the latter case is partly due to the fact that CO emissions decrease with increasing vehicle speed while NOx emissions increase with increasing vehicle speed. These correlations illustrate well the difficulties associated with surrogate calculations for automotive emissions over short averaging times.

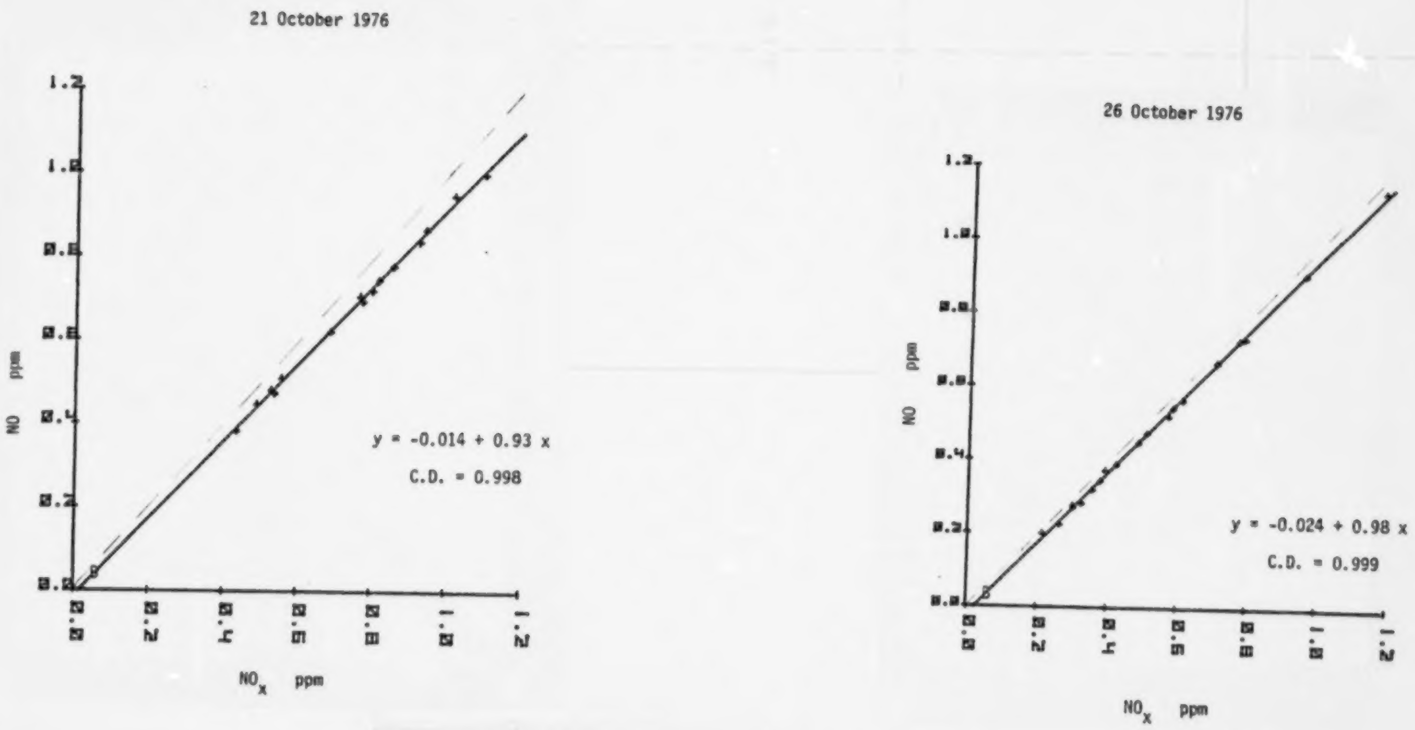

Figure 35. Scatter diagrams comparing the in-roadway NO and NO$_x$ concentrations.

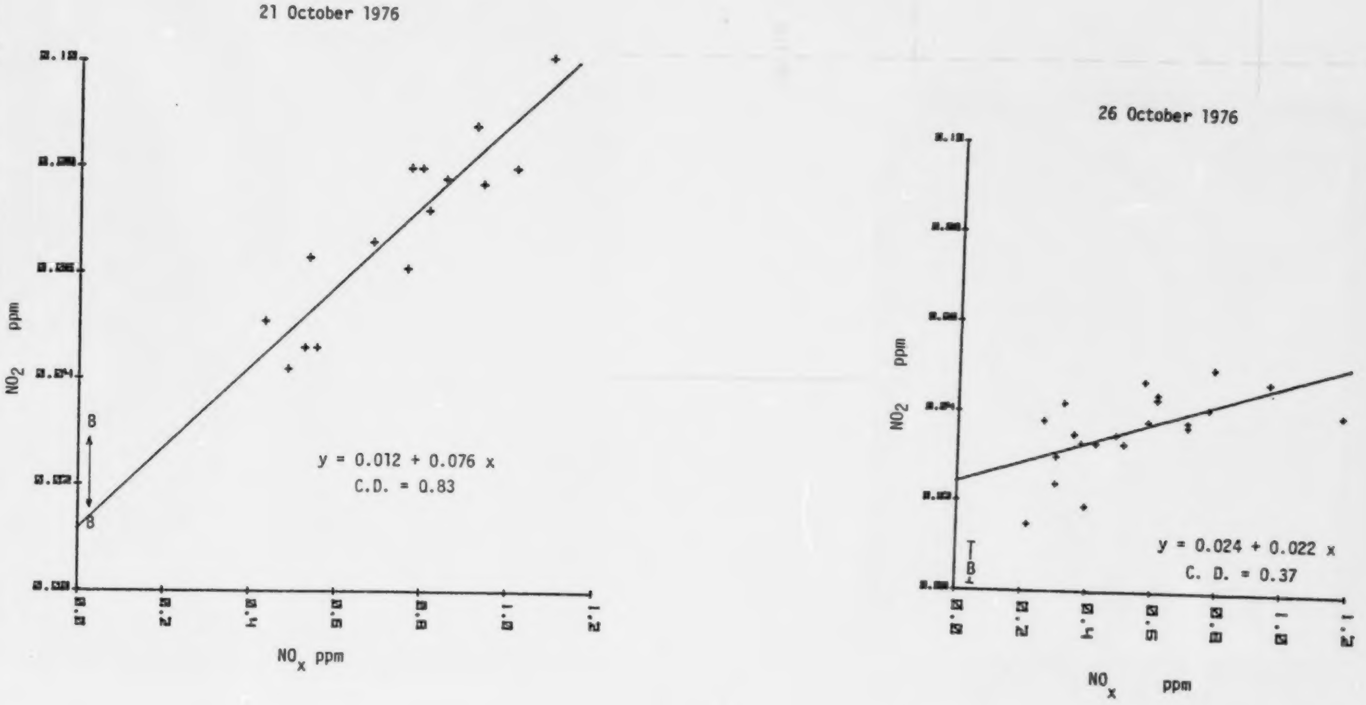

Figure 36. Scatter diagrams comparing the in-roadway NO_2 and NO_x concentrations.

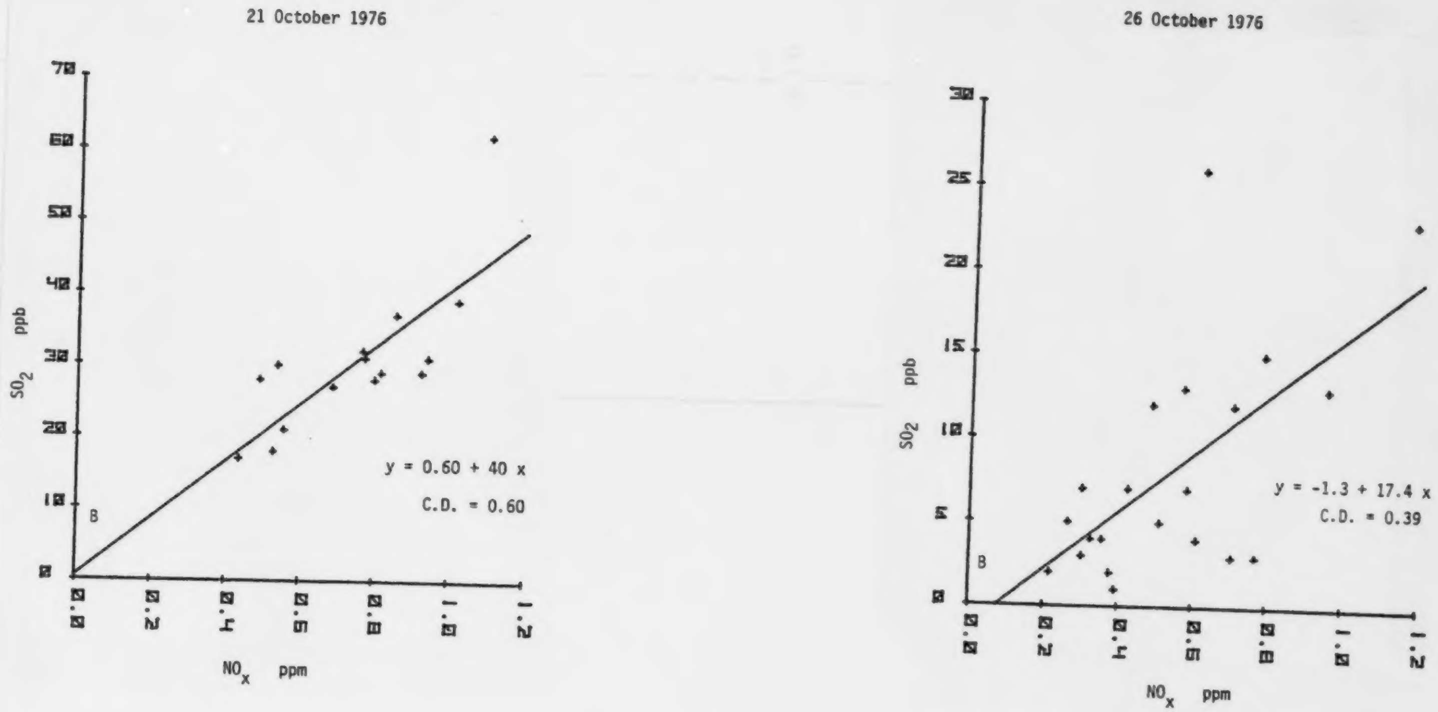

Figure 37. Scatter diagrams comparing the in-roadway Sulfur Dioxide and NO_x concentrations.

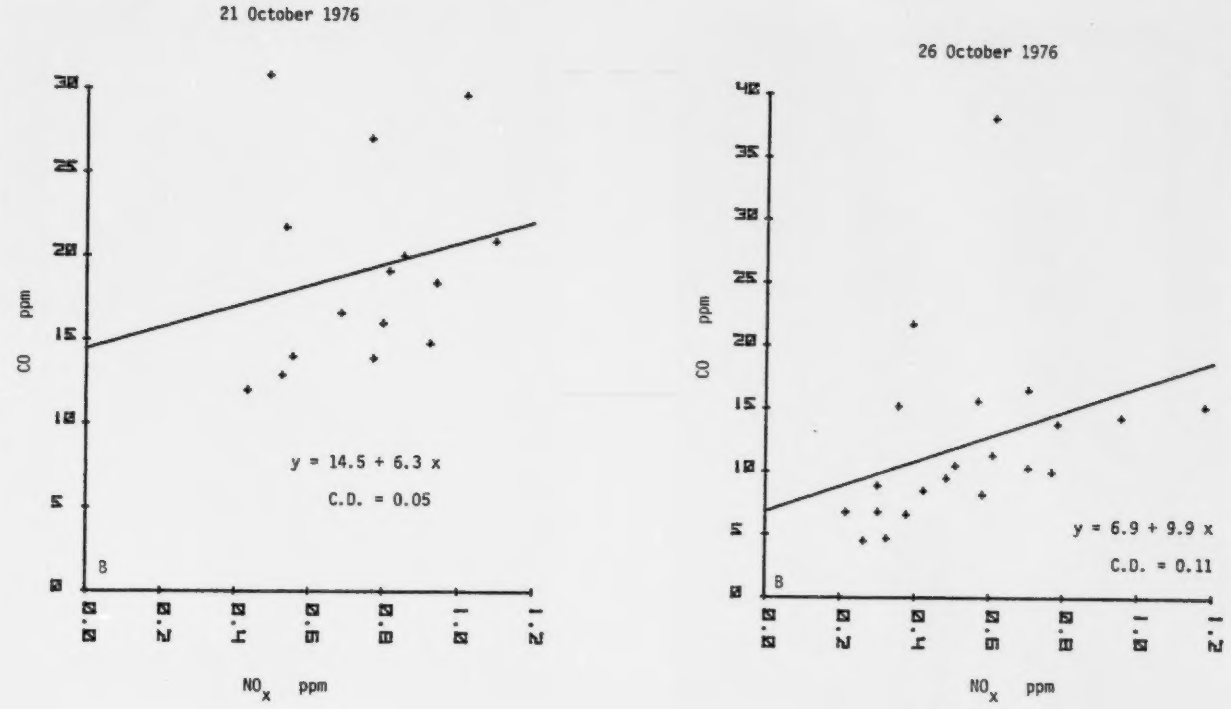

Figure 38. Scatter diagrams comparing the in-roadway Carbon Monoxide and NO_x concentrations.

Figures 39 through 41 show the relation between aerosol concentrations in various size ranges and the NOx concentration. In nearly all cases there is some correlation, but a weak one.

Figures 42 through 51 show scatter diagrams for the daily averages of the in-roadway increments observed for the concentrations of several species. The six days included in these figures are indicated by an asterisk in Table 12, and are Experiments 2, 3, and 7 through 10. To obtain each point, the average background concentrations observed by the University of Minnesota van are subtracted from the average in-roadway concentrations for that day.

The first figures use NOx as the independent variable, for the reasons given above. It is seen that NO correlates very well with NOx in the daily averages, as it did in the individual data points. The other gases do not correlate nearly as well, and again show the risks of using surrogates for estimating the in-roadway concentrations of one pollutant from data for another. The various aerosol size fractions correlate reasonably well with the NOx increments. The non-zero intercept suggests that there is an in-roadway source of NOx which does not emit aerosol.

Figures 49 through 51 have the sulfur dioxide concentration as the independent varible, to see if there is a correlation between the sulfur dioxide and aerosol emissions on the roadway. Reasonable correlations are found, but the correlations are not strong enough to demonstrate a close link between these emissions. The non-zero intercept suggests that if anything, there are in-roadway sources of aerosol which are not strong emitters of sulfur dioxide.

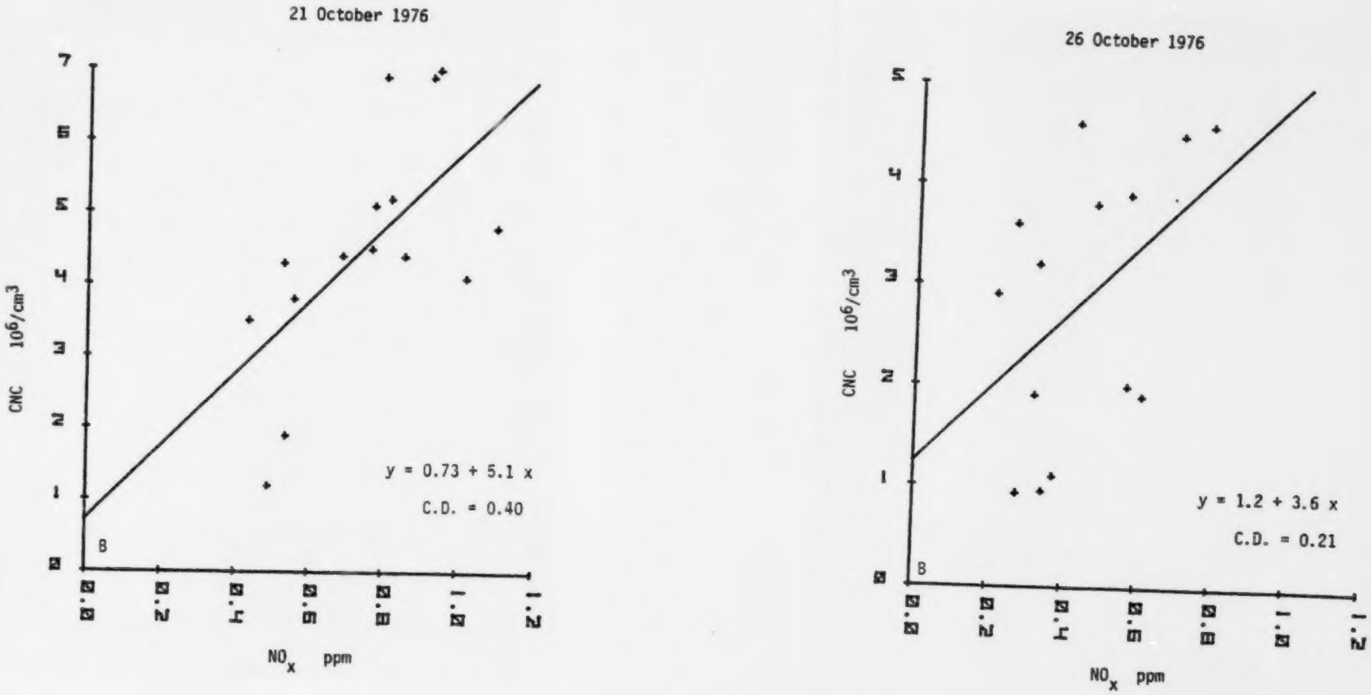

Figure 39. Scatter diagrams comparing the in-roadway Condensation Nuclei and NO_x concentrations.

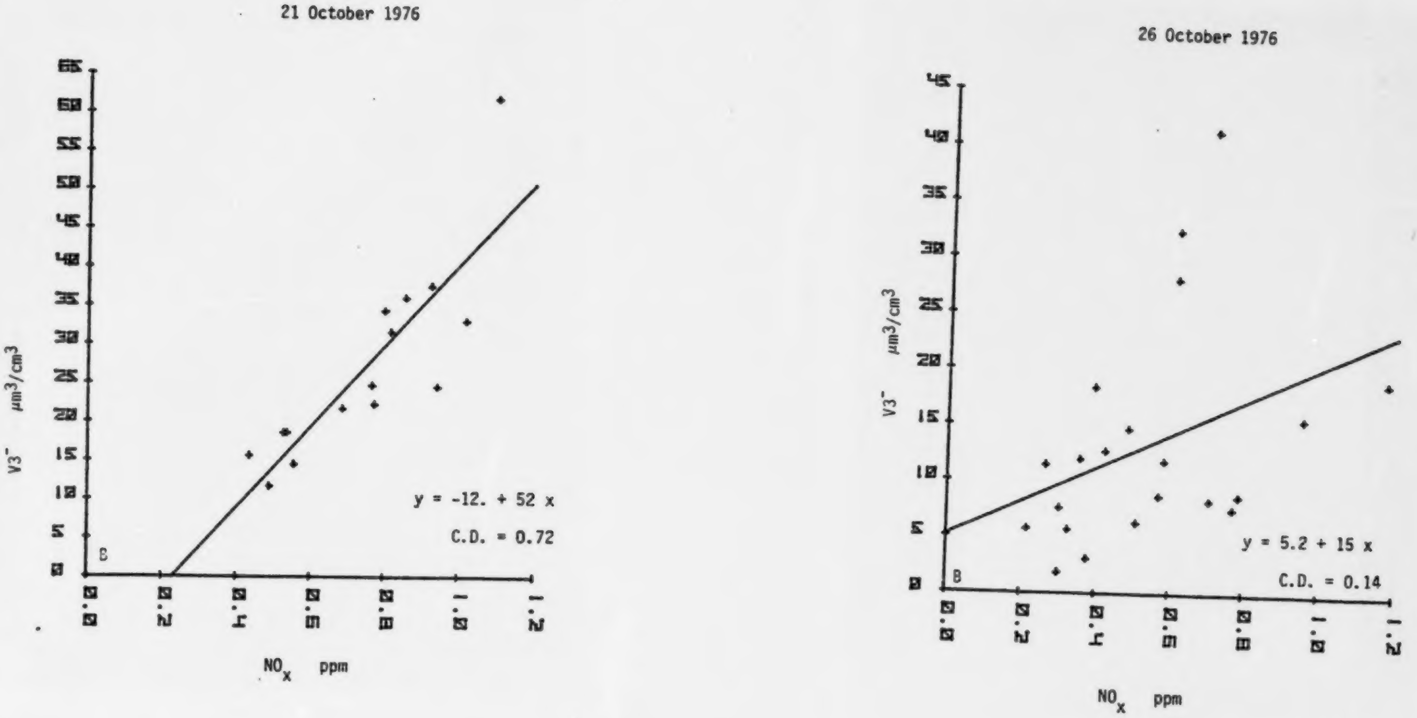

Figure 40. Scatter diagrams comparing the in-roadway submicron aerosol volume and NO_x concentrations.

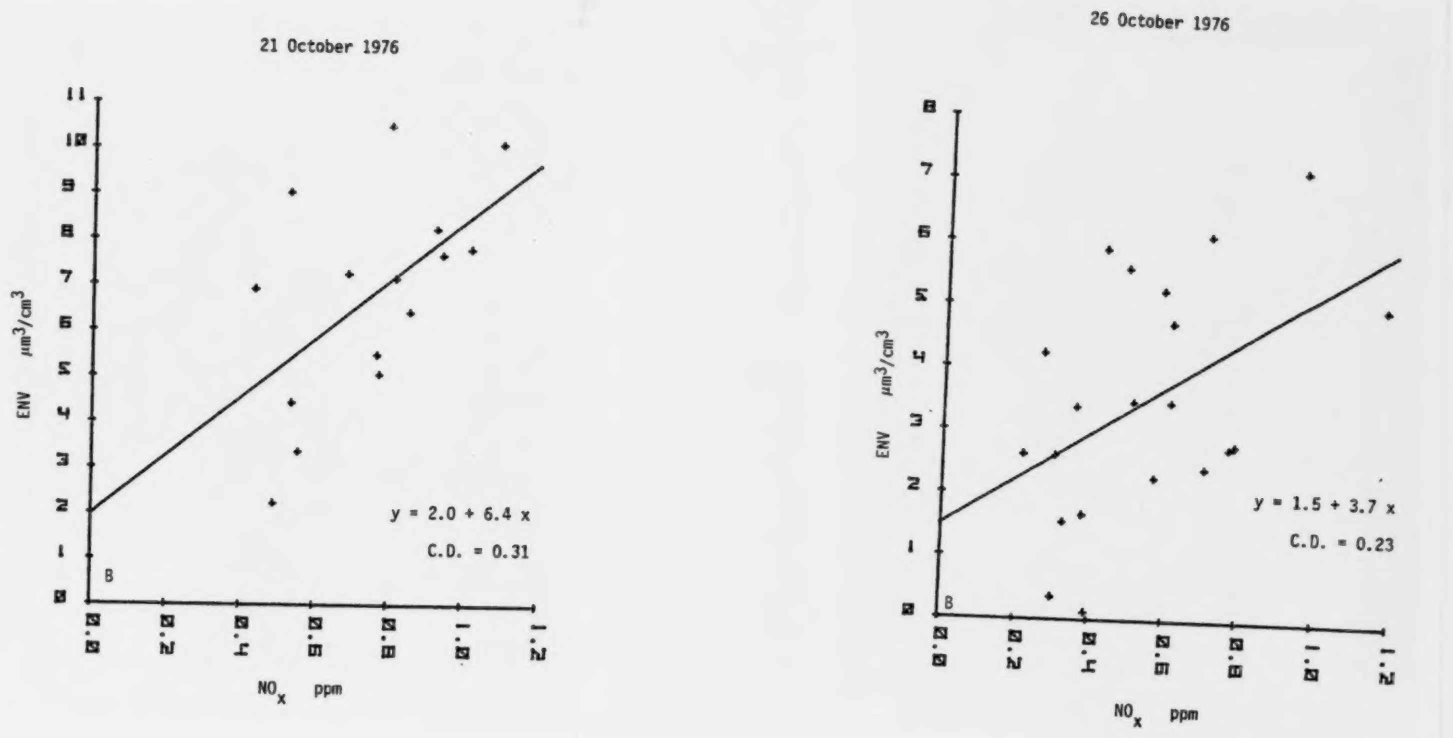

Figure 41. Scatter diagrams comparing the in-raodway estimated nuclei mode aerosol volume and NO_x concentrations.

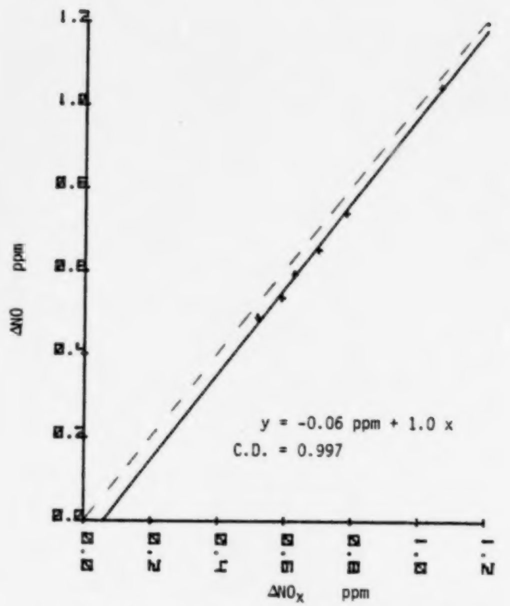

Figure 42. Scatter diagram comparing the daily average in-roadway increments in the NO and NO$_x$ concentrations.

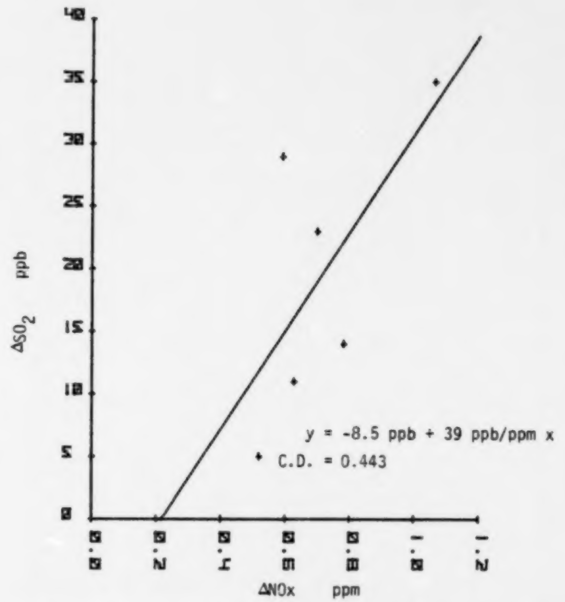

Figure 43. Scatter diagram comparing the daily average in-roadway increments in the Sulfur Dioxide and NO$_x$ concentrations.

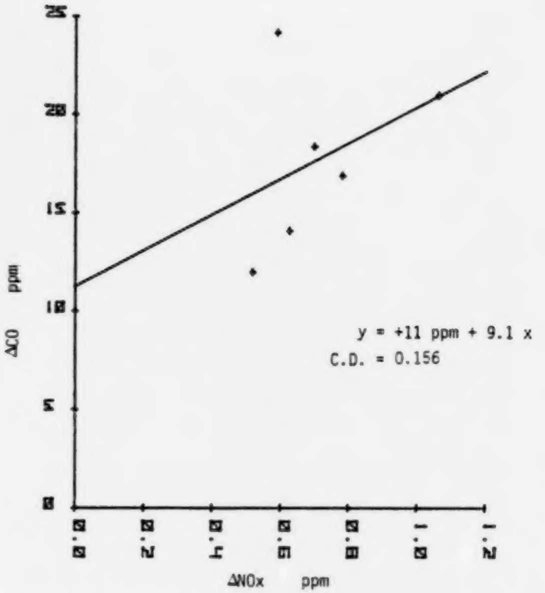

Figure 44. Scatter diagram comparing the daily average in-roadway increments in the Carbon Monoxide and NO_x concentrations.

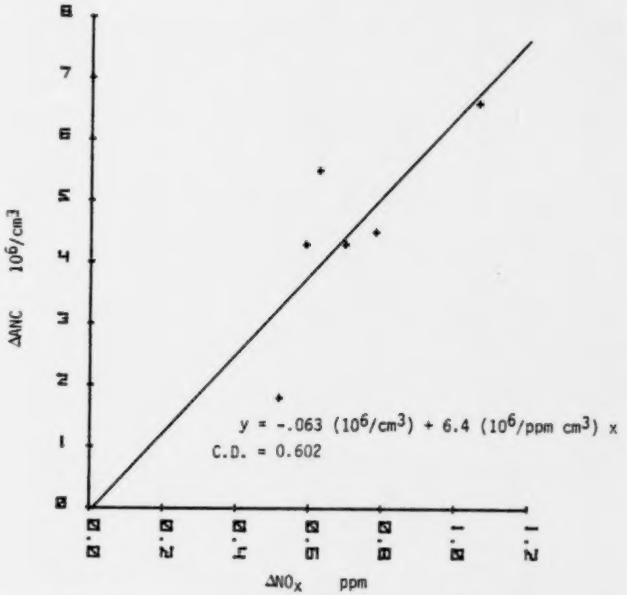

Figure 45. Scatter diagram comparing the daily average in-roadway increments in the Aitken Nuclei and NO_x concentrations.

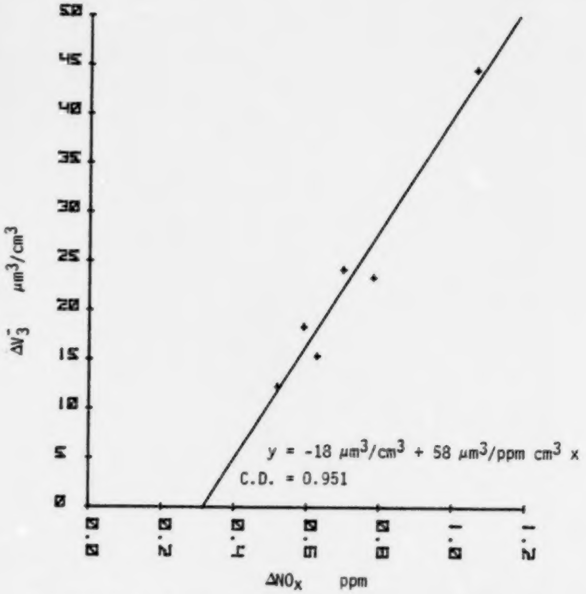

Figure 46. Scatter diagrams comparing the daily average in-roadway increments in the Submicron Aerosol and NO_x concentrations.

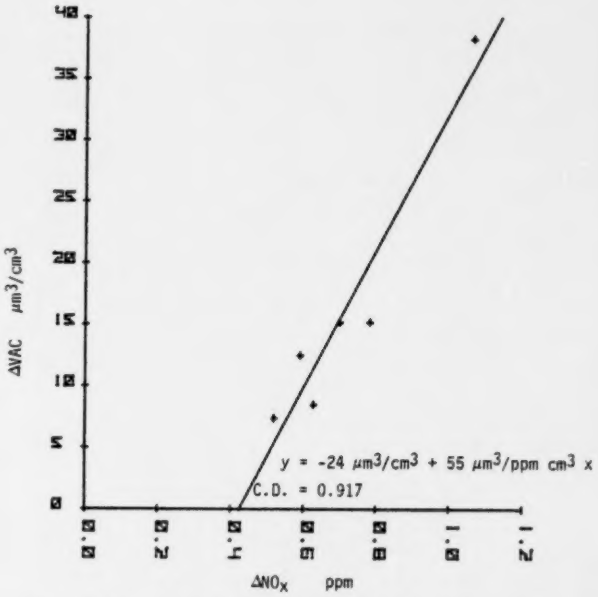

Figure 47. Scatter diagram comparing the daily average in-roadway increments in the Accumulation Mode Aerosol Volume and NO_x concentrations.

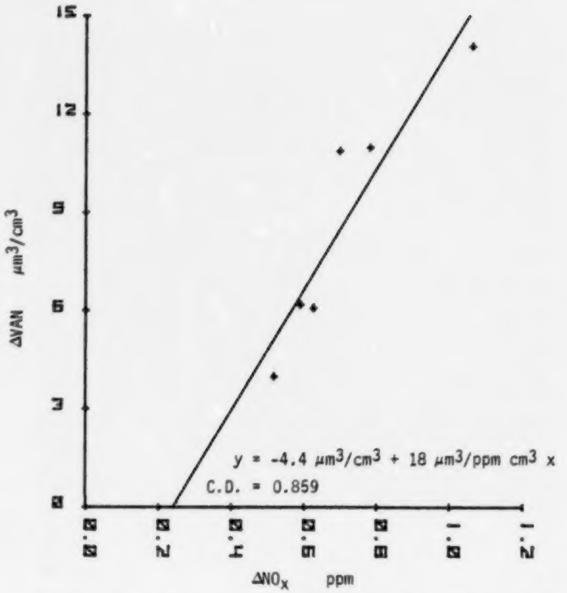

Figure 48. Scatter diagram comparing the daily average in-roadway increments in Aitken Nuclei Aerosol Volume and NO_x concentrations.

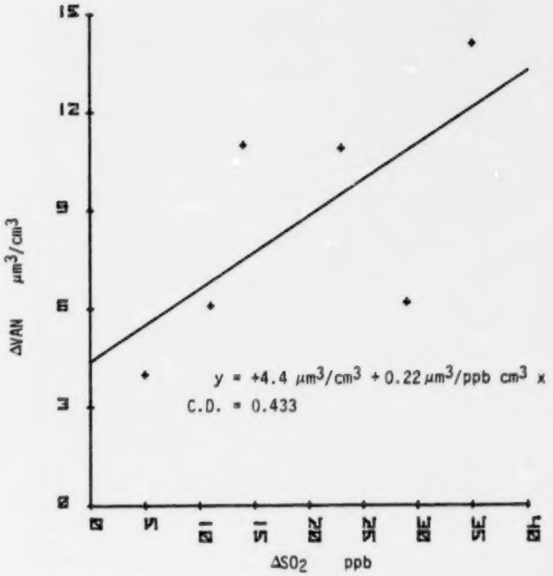

Figure 49. Scatter diagrams comparing the daily average in-roadway increments in the Aitken Nuclei Aerosol Volume and Sulfur Dioxide concentrations.

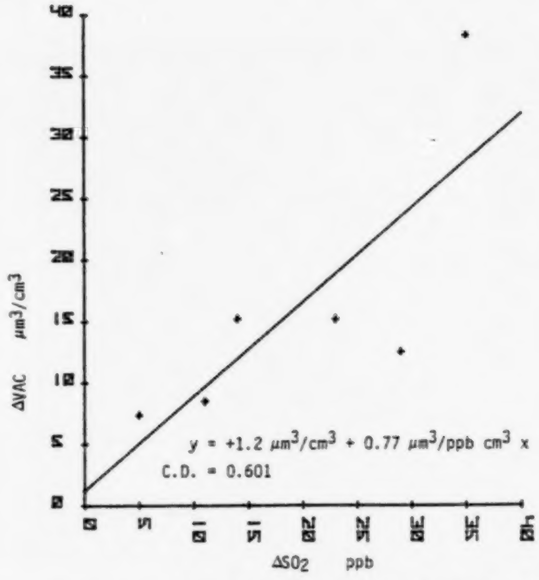

Figure 50. Scatter diagram comparing the daily average in-roadway increments in the Accumulation Mode Aerosol Volume and Sulfur Dioxide concentrations.

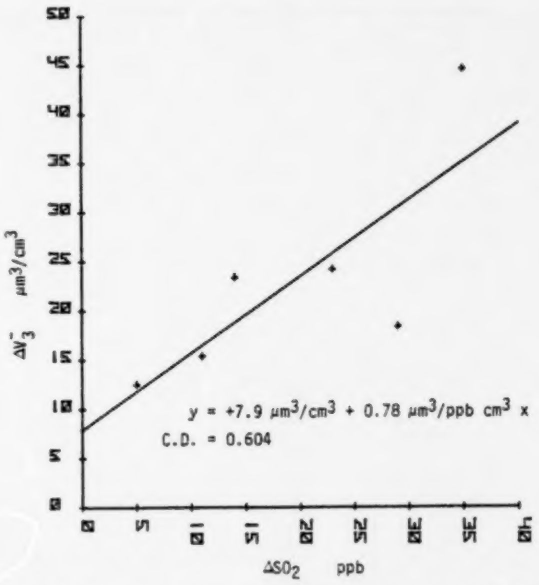

Figure 51. Scatter diagram comparing the daily average in-roadway increments in the Submicron Aerosol Volume and Sulfur Dioxide concentrations.

4.0 OVERVIEW OF THE PLANNED IN-ROADWAY SAMPLING PROGRAM

The following pages give a summary of a planned program to make in-roadway measurements to determine the exposure of vehicle occupants to sulfuric acid or the resulting sulfates emitted from catalyst equipped vehicles. The portions of the program which are discussed include the planned measurement methods, the statistical design on which the sampling strategy is based, and the plans which have been made to implement the program.

4.1 PROGRAM OBJECTIVE

It is the goal of the planned program to develop and implement procedures to measure concentrations of sulfuric acid or sulfates due to catalyst equipped vehicles in such a way that the exposure of people can be reliably estimated, and a determination can be made of the necessity of taking regulatory action to prevent sulfuric acid concentrations from reaching levels that would constitute a hazard to public health.

4.2 MAJOR DESIGN CONSIDERATIONS

The following paragraphs list the considerations which dominated the design of the in-roadway sampling program:

1. The results of the G.M. Sulfate Dispersion Experiments show that the highest concentrations occur on the roadway, so that the population at greatest risk is the vehicle occupants. The present study has chosen to focus on that population;

2. Los Angeles has many multilane freeways with very high traffic densities, and California vehicles are equipped with air pumps and hence, have higher sulfuric acid emission rates than do 49 state cars. As a result, it is expected that Los Angeles will lead the nation in exposure to sulfuric acid or sulfates from catalyst equipped vehicles. In addition, an extensive data base describing trips actually taken in the Los Angeles area is available. Therefore, it is planned to conduct this study in Los Angeles;

3. Atmospheric dispersion models for highways have shown a reasonable correlation with experimental data in cases

where the perpendicular component of the wind velocity is greater than 1 m/sec, but are still not reliable at the low wind velocities, which are the conditions expected to lead to the highest sulfate concentrations. Therefore, at this time, atmospheric dispersion modeling cannot be relied on when making regulatory decisions related to a vehicle sulfate standard. It is necessary to base the decisions on experimental data;

4. Sulfate emission rates from catalyst equipped vehicles are known to be highly variable, both from vehicle-to-vehicle (even within one vehicle model), and for a given vehicle when tested using various driving modes. In addition, it appears that the sulfate emission rates for a given vehicle change significantly as the vehicle ages. Several design considerations follow from these observations:

    A. Sulfate emission rates are variable enough that determining reliable emission factors as a function of vehicle type and driving mode is impossible. At best, emission rates averaged over vehicle populations and test cycles can be obtained;

    B. Sulfate emission rates correlate poorly with emission rates for other pollutants, hence the use of surrogates is not reliable;

    C. A field program must sample the sulfuric acid or sulfate concentrations produced by actual, in-use vehicles, and must include the range of driving modes and traffic situations which do occur. However, it is possible and desirable to design statistical sampling experiments so that little or no data need be collected during times when or at places where it is possible to predict that the probability is small that significant concentrations of emitted sulfates will occur.

5. The present difficulties of modeling atmospheric dispersion when the dispersion is poor and in making detailed predictions of sulfate emission rates from catalyst equipped vehicles both strongly suggest that any field study should be as model free as possible. The use of data from one or a few fixed sites requires considerable modeling to estimate the on-roadway exposure of a population in a major metropolitan area;

6. Based on the most recent emission rate data available, it is thought that the exposures high enough to be of

interest can be divided into two categories. (The dividing line between these categories is not sharp.)

A. High sulfuric acid or sulfate concentrations may occur over extended sections of the roadway when the dispersion conditions are unusually poor. In this situation, many hundreds or even thousands of vehicles contribute to the exposure of a given individual, so exposures should scale in a relatively simple way with the traffic count of catalyst equipped vehicles and the average emission rate of each vehicle;

B. Locally high sulfuric acid or sulfate concentrations may occur behind one or a few vehicles that are unusually strong sulfuric acid sources. Individuals may remain in such local, moving high concentration regions for many minutes, even tens of minutes. These exposures can occur under a more extended variety of meteorologigical conditions than in the above case, and would scale with the distribution of vehicular sulfate emission rates in a different way.

4.3 COMPARISON OF FIXED SITE AND IN-ROADWAY MEASUREMENT STRATEGIES

Since the EPA is already conducting a major monitoring program at a fixed site in Los Angeles to determine the impact of catalyst equipped vehicles, it is important to address the question of why additional measurements might be useful. In part, that question is addressed by the following list of advantages of each measurement strategy. However, the chief reason additional measurements are necessary is that adequate atmospheric dispersion models and sulfate emission rate data do not now exist to use the data from a fixed site to estimate the distribution of exposures people actually are being subjected to in Los Angeles. In addition, it is not reasonable to expect that adequate dispersion models and emission rate data will become available in the next few years.

4.3.1 Advantages of In-Roadway Sampling

1. Data are obtained at the site of the receptor rather than at a nearby site. Therefore, it is not necessary to use an atmospheric dispersion model to transform the data.

2. Models and assumptions are not required to obtain estimates of the distribution functions describing the exposure of the population at risk. This is especially important when dealing with sulfates from catalyst equipped vehicles for which the emission rates are highly variable.

3. The use of statistical, in-roadway sampling eliminates the possibility of bias due to selecting monitoring sites that are not representative. Only in-roadway sampling can explore the full range of vehicle mixes and driving modes which occur in the region of the study.

4. The in-roadway experimental data include the high exposures which result from following one or a few vehicles with unusually high emission rates. This aspect of the exposure which people are now being subjected to cannot be measured at a fixed site.

4.3.2 Advantages of Fixed Site Sampling

1. The subtraction of background concentrations from the observed concentrations is simpler (especially when the wind has an appreciable component perpendicular to the roadway).

2. The data are relatively insensitive to fluctuations in the emissions from individual vehicles, and hence are more easily projected to other vehicle mixes or other average emission rates.

3. Fixed sites can operate unattended, and the logistics of fixed site sampling is generally simpler.

4. It is simpler to obtain long term trends in vehicle emissions by monitoring over a period of years at one or a few fixed sites than it is to obtain similar data from in-roadway experiments.

4.4 OUTLINE OF THE PROPOSED DESIGN

The details of the proposed design of the sampling program and the statistical analysis of the data have been worked out by K. W. Fertig *et al*., and are described in a companion report (Fertig, Mann, and Richards, 1979). A synopsis of that design as well as additional information on the experimental methods are contained in the following text.

It is proposed to use the Los Angeles Regional Transportation Study (LARTS) 1976 data for the population of trips actually taken that year in Los Angeles to construct a statistical sample of trips that can be taken by vans equipped to make measurements of several atmospheric trace constituents. The trip sample probably will be restricted to trips taken between 6 and 11 a.m. in or through the portion of Los Angeles County south of the San Gabriel Mountains and the Santa Susana Mountains. The program will extend for a long enough time to sample a satisfactory range of meteorological conditions. Measurements will be made both on the roadway and at "background" locations somewhat isolated from vehicular traffic, with the roadway and background measurements as closely related in time and space as is practical. The sampling will be biased so that more than a representative fraction of the trips will include freeway driving, and short trips on the smaller city streets will be greatly under represented. Sampling times will be 15 minutes and multiples of 15 minutes. Measured species will include sulfuric acid, total sulfate and ammonia.

The field data will be subjected to a statistical analysis to estimate the distribution functions that describe the exposures of light-duty vehicle occupants which actually took place within the time and geographical boundaries of the field study. The variance of the estimates of these distribution functions will also be calculated. This part of the data analysis will be model free and essentially distribution free.

The data will also be interpreted to estimate the impact of the background ammonia on the observations, and to estimate the distribution functions which might be obtained for other sulfate emission rates. The development of these estimates will require the use of models and simplifying assumptions, but they will have as a point of departure a directly determined (model-free) experimental distribution function for the base year.

4.5 CONSTRUCTION OF TRIP SEQUENCES

It is not practical to sample trips in the LARTS data base in a purely random manner, because the measurement vehicles would spend most of their time on the road going from the end of one trip to the beginning of the next. Therefore, it is planned to construct sequences of trips which do make practical and efficient sampling routes for one measurement team on one day, and then to sample from these sequences according to a statistically sound plan.

4.5.1 Goals

The goals to be achieved in the construction of the trip sequences are as follows:

1. Each sequence is to contain a series of trips from the 1976 LARTS data base which can be efficiently taken by one measurement team in one day;
2. Each sequence should allow time for equipment operation, so atmospheric aerosol samples can be collected to obtain data on observed catalyst related sulfate exposures on each of the trips;
3. The procedures used to construct the sequences, and the information on the properties of the sequences which are tabulated during their construction should be designed in accordance with the requirements of the statistical calculations used to reduce the data.

4.5.2 Proposed Approach

It is proposed to construct a large set of trip sequences (say 10^4 or 10^5 sequences) from the LARTS data base, which will satisfy the criteria listed below. This set of sequences will then form a population which can be sampled in a statistically sound way, with the assurance that the resulting automobile trips can be economically taken. It is planned to bias the sampling, so that the probability of taking trips likely to produce useful data will be increased, and to take this sampling bias into account in the data analysis so that unbiased estimates of the distribution of exposures can be constructed.

4.5.3 Trip Sequence Criteria

The constraints which must be met in the construction of the trip sequences in order to achieve the above goals are as follows:

1. Only a portion of the LARTS data base will be used. The present thinking is to include all trips which start between 0600 and 1059 hours on workdays, and which originate, end, or pass through the region of Los Angeles County south of the San Gabriel Mountains and the Santa Susana Mountains. It is estimated that the LARTS data set contains about 40,000 trips in this subset;
2. Each trip in the selection portion of the LARTS data base will appear in at least one sequence;

3. The number of times each trip in the LARTS data base appears in a sequence will be known. It is desirable to know the number of times each possible pair of trips appears in the same sequence;

4. Each sequence can be driven by one automobile on one day, with adequate time between trips for the driver to perform any operations on the sampling equipment that may be required;

5. The sequences will contain only surface street trips, or only trips which include some freeway travel. (The stratification is still being discussed, and may be modified. The purpose is to provide an operationally and statistically simple means for biasing the sampling in favor of trips which include freeway travel.)

4.5.4 Trip Sequence Construction Procedure

The proposed procedure for constructing the trip sequences is:

1. The region of interest will be divided into a grid of "squares" with a spacing of 2 mi, and the LARTS data base will be sorted into matrices consisting of these grid squares and 20 min time intervals. Two matrices will be constructed, and each will contain all trips of interest. In one matrix, the trips will be sorted according to their origin, and in the other, according to their destination.

2. Sequences will be constructed by selecting a trip, then working backwards and forwards to construct a sequence.

The criteria for selecting connecting trips can include:

1. The time and distance between one destination and the following origin.

2. The number of times the candidate trip is already included in a sequence.

3. The biasing factor, which will cause the more "interesting" trips to be included in a larger number of sequences than other trips. For example, a trip likely to lead to high exposures could be considered interesting.

The sequence of trips constructed by the above procedure will be store in a computer file in such a way that individual sequences can be selected according to the sampling plans as ones to be included in the experimental program.

4.6 MEASUREMENT METHODS

It has yet to be demonstrated in the field that an adequate sulfuric acid measurement method has been reduced to practice. Therefore, the recommendations below are subject to change as the methods development work proceeds. However, it is believed that the present analytical methods for the pollutants of interest are sufficiently well developed that a pilot program can be undertaken to:

1. Complete the selection of the sulfuric acid measurement method.
2. Make measurements over a sample of trip sequences to demonstrate the operability of the sampling plan and provide data on the adequacy of the analytical methods.
3. Greatly expand the existing data base of in-roadway measurements of sulfate concentrations produced by catalyst equipped vehicles.

It is proposed that the field program include, as a minimum, measurements of sulfuric acid and water soluble sulfate in the nuclei mode and accumulation mode particle size range both on the freeway and at the background locations. It is expected that other measurements will be made in the early stages of the field sampling program when the adequacy of the sulfuric acid measurement method is still being demonstrated.

When selecting sulfuric acid measurement methods, it should be remembered that if the data from the October 1976 field program are taken at face value, there was more than enough ammonia in the air at the background site on each sampling day to neutralize the observed excess concentrations of sulfate in the roadway. The effect of the reaction of the emitted sulfuric acid with ammonia is to convert the acid to ammonium bisulfate or ammonium sulfate, and thus to make the emitted sulfate difficult to distinguish from the sulfate due to other sources. As a result, it is essential that the measurement program include the determination of total sulfate concentrations on the roadway and at nearby background sites, and that the precision and accuracy of these data be made as good as possible. In addition, sulfuric acid measurements are also of interest because of the evidence that the acute health effects of sulfuric acid are greater than those of ammonium sulfate.

It is recommended that all sampling on the roadway be done outside the vehicle at the level of the windows or the typical vehicle air inlet. Experimental data obtained in the General Motors Sulfate Dispersion Experiment (Stevens, *et al.*, 1976; Wilson, *et al.*, 1977) show that aerosol concentrations inside vehicles are lower than those outside, so the planned measurements provide an upper limit on the exposure of people to the roadway aerosol. If the observed roadway sulfate concentrations are large enough that there is concern about their health effects, then a study of the relation between the outside and inside aerosol concentrations might be undertaken in a variety of vehicles with a variety of ventilation conditions. Such a study could be conveniently conducted with a dual bag system which simultaneously collects and holds aerosol samples from outside and inside, and an electrical aerosol analyzer which determines the aerosol concentration and size distribution in each bag.

The measurement methods which are recommended at this time for inclusion in the pilot sampling program are as follows.

Sulfuric Acid

Method of choice: low temperature volatilization of sulfuric acid from Teflon filters and determination by a flame photometric detector (FPD). Instrumentation for the implementation of this technique is under development at the Cabot Corporation, and the method is also being characterized and improved at the Environmental Monitoring and Services Center (EMSC). The method has been shown to be sensitive (0.1 ug sulfuric acid per filter) and specific (sulfuric acid can be distinguished from ammonium sulfate and ammonium bisulfate), but the calibration of the present instrumentation with sulfuric acid gives results which vary by a factor of two or three. An ammonia denuder must be used in the collection of filter samples of sulfuric acid, and it is highly desirable to use a size fractionating device so that particles larger than 2 um or 3 um do not reach the filter.

Potential methods: Geomet is currently under contract to the EPA to develop a sensitive (1 um/m3 as sulfuric acid), continuous response instrument that is sensitive to strong acid. The sample air flow is scrubbed of interfering compounds such as SO_2, NO_2, and HCl, and the remaining strong acid (aerosol) contacts a bromide-bromate surface which releases bromine, and the bromine is determined by observing the emission of light from a luminol solution. The usefulness of the instrument depends on the adequate removal in the interfering compounds from the sample air flow.

Progress is also being made in the continuous, *in-situ* measurement of sulfate aerosols by the FPD. The determination of sulfuric acid depends on the difference in the instrument response when the sample air is passed through a tube heated to approximately 80 deg C instead of through an unheated tube.

The Gran titration and the benzaldehyde extraction procedure have also been used for the determination of strong acid or sulfuric acid, but these measurement methods require samples larger than can be collected in 15 minutes.

Sulfate

It is planned to sample ambient air at a rate of 40 to 50 l/min, remove particles larger than 2 um or 3 um with a virtual impactor, and collect the accumulation and nuclei mode aerosol on a 1 um Fluoropore filter, or equivalent. These filters will be transported to the laboratory and analyzed for water soluble sulfate by the ion chromatograph. The detection limit for 15 minute samples is near 0.5 ug/m^3, and the relative standard deviation of the analytical procedure is smaller than 10% for concentrations above about 2 ug/m^3.

Consideration should also be given to the use of the low pressure impactor with flash volatilization into a flame photometric detector for analysis of the impactor stages. These measurements have the purpose of obtaining estimates of the division of the catalyst related sulfate between the nuclei mode and the accumulation mode size particle size ranges.

Ammonia

It is planned to sample ammonia by the two filter method used in the October field program. Ambient air is passed through a Teflon filter to remove all the particulates, then through an oxalic acid coated filter to collect the ammonia gas. The filters are returned to the laboratory and analyzed for ammonium by the ion selective electrode. A sampling flow rate of 40 l/min and present analytical procedures give a detection limit of 2 ug/m^3 for 15 min samples and correspondingly lower limits for longer sampling times. However, there is the possibility that sampling flow rates this high cannot be used if they do not provide adequate time for the ammonia to diffuse to the oxalic acid filter fibers and be collected. Therefore, ammonia sampling times may need to be as long as one hour, but it is known that longer times are not needed.

4.7 SAMPLING EQUIPMENT

The choice of the sampling and analytical methods is still not firm. It is hoped that a package can be designed which can be easily installed in a vehicle without significant vehicle modifications, so that vehicles can be easily added to or released from the program. Because the short sampling times lead to high pumping requirements, consideration is being given to a gasoline engine driven vacuum pump with a capacity of several cubic feet per minute which would be mounted on a roof rack. The filter holders for the various sampling methods could be in the front seat in a package that is secured by the seat belt. Dichotomous samplers would be the ideal equipment for removing the large particles from the sample flow.

Consideration is being given to the use of a tape recorder as a notebook for the driver, a time lapse movie camera to help document driver performance and to understand unusual results, and radios for communication when vans operate in pairs to obtain background data as close as possible to the van obtaining in-roadway data.

4.8 QUALITY ASSURANCE

An in-roadway sampling program conducted in a region of high sulfate concentrations will place extraordinary demands on a quality assurance program. In part, this arises from the fact that the numbers of interest are differences between experimental quantities that are nearly the same. In part, it also arises from the fact that the few high results are of great interest, so a very few erroneously high data points can greatly distort the conclusions. Therefore, a rigorous quality assurance program is recommended.

Quality assurance work should incude:

1. Periodic inspection and independent calibration checks by personnel not otherwise connected to the program;

2. Occasional operation of the samplers in vehicles parked side-by-side;

3. Using an aerosol generator in the field to spike both clean filters and filters which already contain samples. Experiments can be done in which side-by-side samplers collect sulfuric acid, and one of the sample air flows is spiked with known amounts of sulfuric acid aerosol;

4. Quality assurance in the analytical chemistry laboratory, including duplicate analyses of selected extracts, analysis of spiked filters along with

unknowns, etc.

It is frequently true that field programs are run on a schedule which allows minimal time for preparation. Because the need for reliable data is unusually great in this program, it is recommended that adequate time be allowed for demonstrating the dependability of the measurement methods as they will be used before large resources are expended collecting field data.

4.9 THE DATA REDUCTION PROCEDURE

The data reduction procedure has the purpose of combining the experimental data from the in-roadway sampling program so as to obtain Fx(c), which is the function that gives the estimate of the probability that a randomly selected trip taken in Los Angeles will lead to a measured 15 min average concentration of catalyst sulfate of c or more. (A similar estimate will be obtained for one hour averages.) The data reduction procedure to be used is derived and described in detail in a companion report (Fertig, Mann, and Richards, 1979). However, the steps to be used to convert the experimental observations into the desired probabilities are simple enough that they are outlined here.

The first step in the data reduction is to average over any replication, that is, to combine the results when more than one sampler measures the same quantity in one van in one trip. The observed concentrations are next converted into probabilities, and all subsequent calculations are performed with these probabilities. This way of doing things makes it possible to obtain unbiased estimates of the desired probabilities from data for stratified samples without making any assumptions about the mathematical form of the function Fx(c).

When calculating Fx(c) as a function of c, it is necessary to determine one point on the curve at a time. The overall calculation proceeds in three parts:

1. Assume a value for c;
2. Represent the observation for each trip as unity if the maximum 15 min average observed concentration was greater than or equal to c, and zero if it was less than c;
3. Calculate a weighted average of all zeros and ones to obtain the value of Fx(c).

The calculation of the weighted average proceeds as follows:

1. The sampling procedure is biased by including some trips in sequences more often than others, making it more likely that these trips will be taken. This bias is removed by dividing the result (a zero or a one) from each trip by the number of sequences in which the trip appears. The resulting values from a given van on a given day are summed and divided by the sum of the weighting factors;
2. Then the results for all vans on a given day's sampling in the same stratum are averaged without weighting. This average is calculated for each stratum sampled that day;
3. The results from all days in each stratum are averaged without weighting to obtain a result for each stratum;
4. The results from all strata are then averaged together with a weighting factor to obtain the value of Fz(c) at the assumed value of the average concentration c. The weighting factor for each stratum is the fraction of all trips in the portion of the LARTS data base used in this study which fall in that stratum.

These calculations are described by equations 3.1, 3.8, and 3.9 in the report by Fertig, Mann and Richards (1979).

The data reduction procedure also includes calculating the variance of the estimates Fz(c). In addition, the information can be reversed to give estimates of the concentrations that correspond to chosen values of the probability, and again information on the variance of those estimates.

The EMSC chemistry laboratory now uses a computer to reduce and tabulate data from all analyses, so the laboratory data are normally available in computer readable form. A modest amount of programming will make it possible to process the data available at any stage of the measurement program to determine the estimates of the probabilites of various exposures to catalyst related sulfate.

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APPENDIX A

STATISTICAL DESIGN OF AN IN-ROADWAY SAMPLING PROGRAM TO DETERMINE THE EXPOSURE OF AN URBAN POPULATION TO VEHICLE EMISSIONS

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INTRODUCTION

It is known that cars equipped with catalytic converters will emit small amounts of sulfuric acid into the environment. It is the purpose of this report to describe an experimental design which addresses the problem of measuring the exposure of travelers to such emissions. Specifically, persons traveling in or through the Los Angeles area will be considered. Currently, the best available estimates are based on a pollution diffusion model in conjunction with assumed sulfuric acid emissions rates, vehicle densities, meteorological data, and travel data. Horowitz and Papetti [1975] used such information to construct a probabilistic picture of the exposure to H_2SO_4 for persons traveling during peak workday hours (6:00 - 9:00 AM) in the Los Angeles basin. Their results indicate, among other things, that the median one-hour exposure (exposure to H_2SO_4 averaged over one hour) for persons taking trips in Los Angeles during the 6:00 - 9:00 AM peak hours is less than 2 $\mu g/cm^3$, and that 99% of this population will be exposed to 12 $\mu g/cm^3$ or less.

It is the purpose of this experimental design to define an experiment which will estimate these same probabilities using actual field data. That is, no reliance on diffusion models or estimated emission rates will be required. As a consequence, the experiment will produce more reliable estimates of the true H_2SO_4 exposure picture in Los Angeles. The concept is fairly simple. In essence, simulated trips will be taken in the Los Angeles area. Measurement of exposure to H_2SO_4 for each trip will be obtained. These data will then be used to estimate for each exposure level, c, the probability that a trip randomly-selected from the total population of trips will lead to an exposure of c or more. Conversely, this same distribution function can be used to estimate the exposure level, c_ξ, for which the probability is prespecified at ξ that a randomly-selected trip will lead to an exposure level of c_ξ or

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more. The crucial element of the design is obtaining an efficient way to determine what trips the test vehicle should take. Fortunately, an extensive study has been made (and is still being carried on) of the trip patterns within the Los Angeles area. Data were collected by the Los Angeles Regional Transportation Study (LARTS) in 1967 from over 30,000 households in the Los Angeles area as well as actual on-road surveys on what trips were being taken -- their purpose, origin and destination within or through the Los Angeles area. The study was updated in 1976. The data from the original studies have been codified and placed on magnetic tape. The 1967 data were used in the Horowitz and Papetti study. The experimental design that has been constructed proposes to use the 1976 LARTS data set as though it were truly representative of the trip patterns in the Los Angeles basin. Possible consequences of this assumption are discussed in Section 5. It is felt that errors made with such an assumption are quite small relative to the gains in ease of implementation by using an already-codified data set.

In order to proceed with a description of the experimental design, it is appropriate to define the problem precisely. This is done in Section 2. The specific design is given in Section 3. The statistical theory upon which the design is based is presented in Section 4.

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PROBLEM DEFINITION

It is desired to estimate the probability that a randomly-selected trip* taken within or through prescribed boundaries in the Los Angeles basin during a specified time interval will lead to an exposure to H_2SO_4 of a level c or more as a function of c. Thus, we wish to estimate a probability of function, not just one parametric point. Presumably, we are interested in the higher percentiles of this function (those levels of c for which the probability of exceeding are from 0.1 to 0.01 say) so that meaningful control strategies can be developed.

For the following, refer to Figure 2-1. An individual's exposure on a given trip will be defined as his maximum θ-minute average exposure to H_2SO_4 for the trip. Thus, if $[H_2SO_4]_t$ is the concentration the individual sees as a function of time, t, we define his exposure, y, for a trip of length T as

$$y = \sup_{t \epsilon [\Theta, T]} \frac{1}{\Theta} \int_{t-\Theta}^{t} [H_2SO_4]_{t'} dt' , \qquad (2.1)$$

when $T > \Theta$ and

$$y = \frac{1}{\Theta} \int_{0}^{T} [H_2SO_4]_{t'} dt' + [H_2SO_4]_{back} \frac{\Theta - T}{\Theta} , \qquad (2.2)$$

when $T < \theta$. In the above, $[H_2SO_4]_{back}$ is the concentration of H_2SO_4 that would be in the environment if there were no catalyst vehicles. It is estimated from measurements upwind of the freeway and away from major surface streets.

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*Herein, a trip is taken to mean a distinct route in Los Angeles at a particular time.

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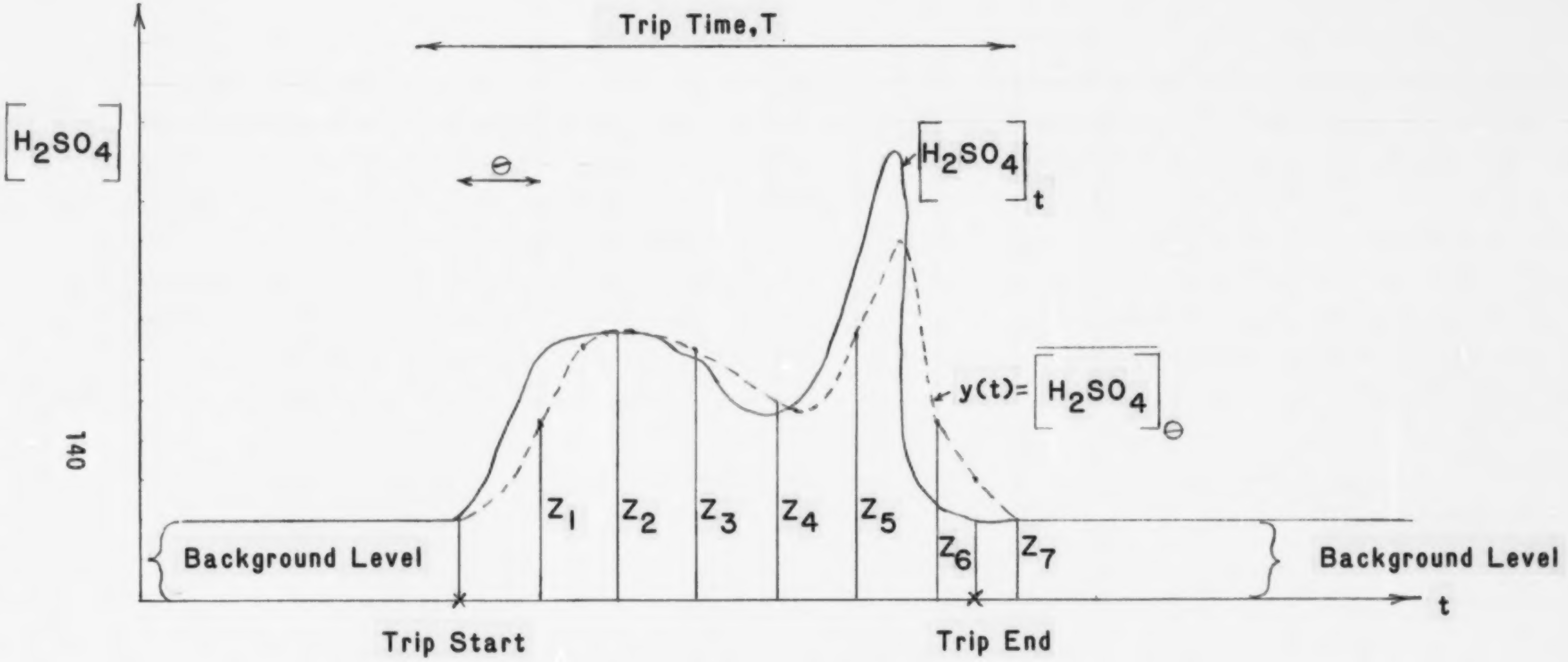

Recorded Value $Z = \text{Max.}(Z_1, \ldots, Z_7)$

$$\doteq \sup_t y(t) \equiv y$$

Fig. 2-1. Concentration, $[H_2SO_4]_t$, versus Time t. Recorded value is Z, which approximates y.

For trips of time, T shorter than Θ, assume $[H_2SO_4]_t = [H_2SO_4]_{\text{Background}}$ for $t > T$.

The variate y is the maximum of a continuous moving θ-minute average exposure. (Ideally, it is the maximum of the dashed curve in Figure 2-1.) This definition is motivated by the relation between maximum exposure to H_2SO_4 and its effect on health. Unfortunately, this variate cannot be measured directly. This is because a continuous record of the concentration profile for a given trip cannot feasibly be measured. At best, a 15-minute average exposure is measurable. Thus, the variate y for any trip will be approximated by the maximum θ-minute average as determined from a set of 15-minute averages taken consecutively during the trip. For example, it is the maximum of $(Z_1, Z_2, \ldots Z_7)$ given in Figure 2-1.

It is expected that two values of will be of interest for the determination of health effects. These are $\theta = 15$ minutes and $\theta = 60$ minutes. If the trip is shorter than 15 minutes, then Eq. (2.2) applies for both values of . In such cases the above method of being able to measure only 15-minute averages presents no problem. This is because the actual exposure as defined by Eq. (2.2) is measured in the $\theta = 15$ minute case or can be inferred by adding on 45 minutes of measured background in the $\theta = 60$ minute case.

For a given value of θ, let $\overline{F}_y(c)$ be the probability that a randomly-selected trip taken in Los Angeles will lead to a maximum exposure to H_2SO_4 of c or more. From the above, the variate y will be approximated by the maximum θ-minute average as determined from consecutively measured 15-minute average exposures. Call this latter measured maximum, z. Let $\overline{F}_z(c)$ be the probability that a randomly-selected trip in Los Angeles will lead to a measured maximum exposure of c or more. Even if we discount as minor the differences between y and z due to not being able to record the continuous concentration profile, there will in general be a difference between $\overline{F}_y(c)$ and $\overline{F}_z(c)$ because the variate z includes analytical measurement error as a source of variation. These latter errors are discussed in further detail in the appendix. There it is shown that $\overline{F}_z(c)$ and $\overline{F}_y(c)$ are related by

$$\overline{F}_z(c) = \overline{F}_y(c)(1+B) \quad , \qquad (2.3)$$

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where B is a bias term equal to about 0.0080/L where L is the number of replicate measurements used in the determination of z. Replicate measurements can be obtained by placing more than one sampler in a vehicle. Since this difference is considered small, it is sufficient to use an estimate of $\bar{\bar{F}}_z(c)$ as a proper description of the H_2SO_4 exposure picture in Los Angeles.

The function $\bar{\bar{F}}_z(c)$ is to be estimated for a specified set of days, D. (For example, D = set of all workdays in 1978.) Without the use of forecasting models, this set of days must be restricted to those that can be sampled (non-future days).

The function $\bar{\bar{F}}_z(c)$ can be written in terms of the functions $\bar{\bar{F}}_z(c|d)$, the probability that a randomly-selected trip will lead to a measured exposure greater than or equal to c for a given day d. (The notation P(A|B) refers to the probability of event A given event B.) Thus, if N_d represents the number of trips taken in Los Angeles on day d ($N_d \simeq 15\times10^6$), then

$$\bar{\bar{F}}_z(c) = \sum_{d\varepsilon D} \frac{N_d}{N_T} \bar{\bar{F}}_z(c|d) \quad , \qquad (2.4)$$

where $N_T = \sum_{d\varepsilon D} Nd$ is the total number of trips taken in Los Angeles over all days in D. If one is willing to assume N_d is essentially constant, we have

$$\bar{\bar{F}}_z(c) = \sum_{d\varepsilon D} \bar{\bar{F}}_z(c|d)/M \quad , \qquad (2.5)$$

where M is the number of days in D. In the subsequent discussion, it will be assumed that N_d is constant. The statistics generated are easily extended to the case where one has estimates of N_d/N_T.

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Equation (2.5) provides the method to estimate $\bar{F}_z(c)$. Essentially, one randomly chooses days from D with prescribed probabilities. For each day chosen, test vehicles are sent out on the roadways within the geographical boundaries of interest. Their routes will be determined by selected trips from the LARTS data set with prescribed probabilities. The observations will be combined for each day to form an estimate, $F_z(c|d)$, of the probability that a randomly-selected trip will lead to an H_2SO_4 exposure of c or better for each day d. These latter functions may then be combined to obtain an estimate $\hat{\bar{F}}_z(c)$ or $\bar{F}_z(c)$. The next section gives the details of this procedure.

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SAMPLING DESIGN AND STATISTICS USED

Let U_d be the set of trips about which inferences are to be made on the dth day. Without any further information, we will consider U_d is represented by the LARTS data set. That is, it is assumed that the statistics one can obtain based on the LARTS data set are essentially the same as one would obtain from U_d.

Consider obtaining a simple random sample from U_d of size n. Without any restriction on the sampling procedure, it might take as many as 2n test vehicles to obtain exposure measurements for each trip as well as background data. Furthermore, once one vehicle is through with gathering its data for one trip, it may become inactive. This would be quite cost-ineffective. It is far preferable to generate a sequence of trips from U_d that one car can efficiently take. If such a sequence is generated for each of K pairs of cars, then there would be optimum use of driver time, the main cost component in gathering the samples. The proposed sampling design is to do just that. We let S be a set of feasible sequences of trips. Thus, each $s \in S$ is a set of trips $\{u_1^d, \ldots, u_{n_s}^d\}$ that are compatible with one another in the sense that one car can take all the trips in s. For example, trips that occur at the same time cannot be included in one sequence, s. In order to reduce the cost of obtaining the samples, each trip in the sequence should end relatively near the origin of the next trip. An algorithm to generate a set S is currently being constructed. The most important property S must have is that it contain every trip in U_d in at least one s.

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The proposed experimental design is to obtain a sample, s_k from S for each of K pairs of cars ($K \simeq 4$). While one car in each pair is taking a trip $u \varepsilon s_k$, the other car is obtaining background H_2SO_4 levels for that trip. If the number of trips in s_k is n_{s_k}, then the number of trips taken on the dth day for the K pairs of cars is $\sum_{k=1}^{K} n_{s_k}$.

It is expected that trips that do not involve the freeway will lead to very low levels of exposure. For the levels of c of interest ($\bar{F}_y(c) \simeq 0.1$ say), it is highly probable that surface street trips will not lead to measured exposures greater than such c. In order to obtain the more interesting data and consequently reduce the errors in the estimates, it is therefore proposed to stratify the set U into two sets:

$$U_{d1} = \left\{ u \varepsilon U_d \,|\, u \text{ does not use the freeway} \right\} \quad ,$$

$$U_{d2} = \left\{ u \varepsilon U_d \,|\, u \text{ uses the freeway} \right\} \quad .$$

The sequence set S will be constructed to reflect this stratification. Thus, we let

$$S_1 = \left\{ s \,|\, s \text{ contains trips from } U_{d1} \text{ only} \right\} \quad ,$$

$$S_2 = \left\{ s \,|\, s \text{ contains trips from } U_{d2} \text{ only} \right\} \quad ,$$

and $S = S_1 \cup S_2$ is the union of S_1 and S_2. By this process, we limit any one pair of cars to take only surface street trips or only freeway trips on any given day. The actual approtionment will involve estimates of the variances obtained in each stratum. The details are given later in this section.

In what follows we will construct a step-by-step procedure to estimate the distribution function $\bar{F}_z(c)$. In essence, this will be done by estimating the probability, $\bar{F}_{jz}(c|d)$, that a randomly-selected trip in the jth stratum on a sampled day, d, will lead to an exposure of c or more (Eq. (3.1) below). These estimates will be combined for each day d sampled to provide an estimate of $\bar{F}_{jz}(c)$, the probability that a randomly-selected trip in the jth stratum for the entire set, D, will lead to an exposure of level c or more (Eq. (3.8) below). Finally, the estimates of $\bar{F}_{jz}$ (c) for the strata are combined according to the number of trips in each stratum to yield an estimate of $\bar{F}_z(c)$, the overall probability that randomly-selected trips taken some time in D will lead to an exposure of c or more (Eq. (3.9) below).

It should be noted that the primary estimation is performed in the probability space rather than in the exposure space. This is done because of the ease of obtaining unbiased estimates in this space without the requirement of simple random sampling. For each level c, the data z are transformed into 0-1 variates according to whether or not they fail to exceed c. This is done through the use of the indicator function defined in (3.2) below.

For the moment, consider just one stratum indexed by the subscript j. We seek an estimate of $\bar{F}_{jz}(c|d)$ for this stratum. This is the probability a randomly-selected trip in U_{dj} will lead to a measured exposure of c or better on the dth day. Section 4 provides a general theory to construct such estimates. From that theory, we obtain

$$\hat{\bar{F}}_{jz}(c|d) = \sum_{k=1}^{K_{dj}} \left[\sum_{u \varepsilon s_k} \left(I(z_{ud.} - c)/g_{ju} \right) \Big/ \sum_{u \varepsilon s_k} 1/g_{ju} \right] \Big/ K_{dj} \qquad (3.1)$$

where $\sum_{u \varepsilon s_k}$ indicates summation over all trips in the sample sequence s_k for the kth car,

$$I(x) = \begin{cases} 1 & x > 0 \\ 0 & x < 0 \end{cases} , \qquad (3.2)$$

K_{dj} is the number of pairs of cars sampled from the jth stratum on day d, and

$$z_{ud.} = \sum_{\ell=1}^{L_{ud}} z_{ud\ell}/L_{ud} \qquad (3.3)$$

is the average over L_{ud} replicate measurements for trip u in s_k. Because of the constraints of sampling with a fixed number of cars, the $z_{ud.}$ are not independent random variables. The weights g_{ju} are therefore necessary to unbias the estimate. In particular, g_{ju} is the number of sequences in S_j that contain the trip u. Thus

$$g_{ju} = \sum_{s \varepsilon S_j} \delta_{su} \qquad (3.4)$$

where

$$\delta_{su} = \begin{cases} 1 & u \varepsilon s \\ 0 & u \not\varepsilon s \end{cases} . \qquad (3.5)$$

From (3.1), we see $\hat{\bar{F}}_{jz}(c|d)$ is defined as a weighted average of zero-one random variates (the $I(z_{ud.} - c)$). It is shown in Section 4 (Eq. (4.8)) that in order for the g_{ju} to be the proper unbiasing constants, each sequence s_k in S_j that is sampled must be chosen with probability

$$p_j(s_k) = \frac{1}{N_{dj}} \sum_{u \varepsilon s_k} 1/g_{ju} \quad , \tag{3.6}$$

where N_{dj} is the number of trips in U_{dj}. The function $p_j(\cdot)$ defined on S_j is referred to as the sampling design for the jth stratum. It is a true probability function in that $p_j(s_k) > 0$ and $\sum_{s_k} p_j(s_k) = 1$.

The estimate given by (3.1) is an unbiased, location-scale invariant, distribution-free estimate of $\bar{F}_{jz}(c|d)$. The unbiased property implies

$$E\left(\hat{\bar{F}}_{jz}(c|d)\right) = \bar{F}_{jz}(c|d) \quad , \tag{3.7}$$

where $E(\cdot)$ is the expectation operator. The invariance property means, among other things, that if we had estimated $1 - \bar{F}_{jz}(c|d) = F_{jz}(c|d)$, the probability that the measured exposure of a randomly-selected trip in the jth stratum will be less than c on the dth day based on $1 - I(z_{ud.} - c)$, we would find $\hat{F}_{jz}(c|d) = 1 - \hat{\bar{F}}_{jz}(c|d)$. Thus, it is irrelevant which way the data are considered.

We now assume that day d is selected from D purely randomly. The estimate of $\hat{\bar{F}}_{jz}(c)$ is then defined as

$$\hat{\bar{F}}_{jz}(c) = \sum_{d=1}^{m_j} \frac{1}{m_j} \hat{\bar{F}}_{jz}(c|d) \quad , \tag{3.8}$$

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where m_j is the number of days for which stratum j was sampled. This is just the simple average of the $\hat{F}_{jz}(c|d)$ over the days sampled. The estimates of the J strata are combined via

$$\hat{F}_z(c) = \sum_{j=1}^{J} \lambda_j \hat{F}_{jz}(c) \tag{3.9}$$

with $\lambda_j = N_j/N$. Here N_j is the number of trips in U_j and $N = \sum_{j=1}^{J} N_j$. The set U_j equals the union of the U_{dj} over all days. Again, Eq. (3.9) is just a weighted average of the $\hat{F}_{jz}(c)$. The weighting factor λ_j can be regarded as the probability that a trip randomly selected from the population of trips U is in the jth stratum.

Consider the specific case where four pairs of cars are available for each day (K = 4). Let $t_i = (K_{i1}, K_{i2})$ represents an allocation of cars on any day with K_{i1} pairs of cars sampling from stratum 1 (surface streets) and K_{i2} pairs of cars sampling from stratum 2 (freeways). Because we are interested mostly in freeway trips but also want to be able to estimate the variances and covariances of the estimators $\hat{F}_{jz}(c)$ for j = 1 and 2, we will restrict ourselves to $t_1 = (0,4)$ and $t_2 = (2,2)$. Thus, on any day, either all four pairs of cars will be sent out on the freeway or two pairs will be sent on the surface streets and two pairs on the freeway. If m is the number of days sampled in D, v_1 is the number of days allocation t_1 is used, and v_2 is the number of days allocation t_2 is used, the optimum set of v's that minimize the variance of $\hat{F}_z(c)$ are given by

$$\frac{v_2}{m} = \frac{\lambda_1}{\lambda_2} \left[\frac{\overline{\sigma^2_{kd1}}/2 + \sigma^2_{d1}}{\overline{\sigma^2_{kd2}}/4} \right]^{1/2}_{12} , \tag{3.10}$$

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and

$$v_1 = m - v_2 \quad ,$$

where

$$\sigma^2_{dj} = \sum_{d=1}^{M} \left(\bar{\bar{F}}_{jz}(c|d) - \bar{F}_{jz}(c)\right)^2 \Big/ (M-1) \quad , \tag{3.11}$$

$$\overline{\sigma^2_{kdj}} = \sum_{d=1}^{M} \mathrm{var}[\hat{\bar{\bar{F}}}_{jkz}(c|d)]/M \quad , \tag{3.12}$$

with

$$\hat{\bar{\bar{F}}}_{jkz}(c|d) = \left(\sum_{u \in s_k} I(z_{udk.} - c)/g_{ju}\right) \Big/ \sum_{u \in s_k} 1/g_{ju}$$

being the estimate of the probability of exceeding c based on data from the kth car on day d. The variance term σ^2_{dj} measures the variability between days of the probability that a randomly-selected trip will lead to an exposure of c or more. The term $\overline{\sigma^2_{kdj}}$ is the average over all days of the variance of the estimator based on a randomly-chosen sequence, s_k (random according to $p(s_k)$). The variance of this estimator is given by

$$\begin{aligned} \mathrm{var}\hat{\bar{\bar{F}}}_{jkz}(c|d) = {} & \sum_{s_k \in S_j} p_j(s_k) \sum_{u \in s_k} p_{ud}(1 - p_{ud}) \Big/ \left[g^2_{ju} \Big/ \left(\sum_{u' \in s_k} 1/g_{ju'} \right)^2 \right] \\ & + \sum_{s_k \in s_j} p(s_k) \left[\sum_{u \in s_k} (p_{ud}/g_{ju}) \Big/ \left(\sum_{u' \in s_k} 1/g_{ju'} \right) \right]^2 \end{aligned} \tag{3.13}$$

with p_{ud} representing the true probability that the trip $u \varepsilon U_d$ will lead to a measured exposure of c or better on the dth day.

In Eq. (3.10) $\overline{\sigma^2_{kd1}}$ and σ^2_{d1} will tend to be very small relative to $\overline{\sigma^2_{kd2}}$. This is because $\bar{\bar{F}}_{jz}(c|d)$ for $j = 1$ is essentially zero for each day, d. As an example, suppose it is estimated that $(\overline{\sigma^2_{kd1}}/2 + \sigma^2\ )/\overline{\sigma^2_{kd2}} \simeq 1/100$. For the Los Angeles County morning trips $\lambda_1/\lambda_2 \simeq 3/2$. Thus, if $m = 200$ days,

$v_1 = 170$ days

$v_2 = 30$ days

That is, 170 of the 200 days, all four pairs of cars should be sent on the freeway. For 30 of the 200 days, two pairs should go on the surface streets and two pairs on the freeway. This allocation assumes that the 200 days were selected randomly from D and that the 30 t_2 type allocations are distributed randomly among these, with the remaining 170 t_1 type allocations going to the rest.

3.1 Variance Estimates

The variance of $\hat{\bar{\bar{F}}}_z(c)$ is given in Section 4, Eq. (4.28), as

$$\text{var}\hat{\bar{\bar{F}}}_z(c) = \sum_{j=1}^{J} \lambda_j^2 \text{var}\hat{\bar{\bar{F}}}_{jz}(c) + \sum_{j}\sum_{\neq j'} \lambda_j \lambda_{j'} \text{cov}\left(\hat{\bar{\bar{F}}}_{jz}(c), \hat{\bar{\bar{F}}}_{j'z}(c)\right) , \quad (3.1.1)$$

where J is the number of strata. In order that (3.1.1) be useful, each variance-covariance term must be defined. The variance of $\hat{\bar{\bar{F}}}_{jz}(c)$ is derived in Section 4, Eq. (4.31) and (4.32). For the case considered here, it is

$$\mathrm{var}\hat{\bar{F}}_{jz}(c) = \frac{1}{m_j}\left[\sum_{d\varepsilon D} \mathrm{var}\bar{F}_{jkz}(c|d)/M\right]$$

$$\cdot \sum_{i=1|t_i \ni j}^{R} (v_i/K_{ij})/m_j + \frac{1}{m_j}\left(1 - \frac{m_j}{M}\right)$$

$$\cdot \frac{1}{M-T} \sum_{d\varepsilon D} \left(\bar{F}_{jz}(c|d) - \bar{F}_{jz}(c)\right)^2 \quad , \qquad (3.1.2)$$

where R is the number of different allocations used, v_i is the number of days that allocation type t_i is used; m_j is the total number of days stratum j is sampled, and K_{ij} is the number of pairs of cars used for stratum j in allocation t_i. The notation $i = 1 | t_i \ni j$ refers to summation over all indexes i such that allocation t_i sends at least one pair of cars into stratum j ($K_{ij} > 0$).

Note that the variance expressed in (3.1.2) has two components. The first reflects the uncertainty of the estimator for any given day averaged over all days. The second represents the natural variability in the population from day to day. The variance in (3.1.2) can be estimated from the data at hand via

$$\widehat{\mathrm{var}}\left(\hat{\bar{F}}_{jz}(c)\right) = \frac{1}{m_j}\left(1 - \frac{m_j}{M}\right) \sum_{d\varepsilon q_j} \left(\hat{\bar{F}}_{jz}(c|d) - \hat{\bar{F}}_{jz}(c)\right)^2/(m_j - 1)$$

$$+ \sum_{d\varepsilon q_j} \sum_{k=1}^{K_{dj}} \left(\hat{\bar{F}}_{jkz}(c|d) - \hat{\bar{F}}_{jz}(c|d)\right)^2/(K_{dj} - 1)$$

$$\cdot \left\{\frac{1}{Mm_j}\left(\sum_{i=1|t_i \ni j}^{R} v_i/K_{ij}\right)\right\} \quad , \qquad (3.1.3)$$

where q_j is the set of days sampled for stratum j. This has expected value $\mathrm{var}\left(\hat{\bar{F}}_{jz}(c)\right)$. (See Section 4, Eqs. (4.34) through (4.40).)

The covariance between $\hat{\bar{F}}_{jz}(c)$ and $\hat{\bar{F}}_{j'z}(c)$ is

$$\mathrm{cov}\left(\hat{\bar{F}}_{jz}(c),\hat{\bar{F}}_{j'z}(c)\right) = \sum_{d\varepsilon D}\left(\bar{F}_{jz}(c|d) - \bar{F}_{jz}(c)\right)\left(\bar{F}_{j'z}(c|d) - \bar{F}_{j'z}(c)\right) \cdot \frac{1}{M}\left(\frac{Mm_{jj'} - m_j m_{j'}}{m_j m_{j'}(M-1)}\right) , \qquad (3.1.4)$$

with $m_{jj'}$ being the number of days both stratum j and stratum j' are sampled together. For the case mentioned above with $K = 4$, $t_1 = (0,4)$, $t_2 = (2,2)$, we have $m_{jj} = v_2$, the number of days allocation t_2 is used. The above covariance (3.1.4) can be estimated from

$$\widehat{\mathrm{cov}}\left(\hat{\bar{F}}_{jz}(c),\hat{\bar{F}}_{j'z}(c)\right) = \frac{Mm_j m_{j'}}{Mm_{jj'} - m_j m_{j'}} \frac{1}{m_{jj'} - 1} \sum_{d\varepsilon q_{jj'}} \left(\hat{\bar{F}}_{jz}(c|d) - \hat{\bar{F}}^{*}_{jz}(c)\right) \cdot \left(\hat{\bar{F}}_{j'z}(c|d) - \hat{\bar{F}}^{*}_{j'z}(c)\right) , \qquad (3.1.5)$$

with $q_{jj'}$ being the set of days for which both stratum j and j' are sampled and $\hat{\bar{F}}^{*}_{jz}(c)$ is the estimate for $\bar{F}_{jz}(c)$ based on those days only. The above was constructed so that it has expectation $\mathrm{cov}(\hat{\bar{F}}_{jz}(c),\hat{\bar{F}}_{j'z}(c))$. Again, see Section 4, Eqs. (4.41) through (4.46).

The estimates given in Eqs. (3.1.3) and (3.1.5) can be used in Eq. (3.1.1) to obtain an unbiased estimate of the variance of $\hat{\bar{F}}_z(c)$.

Since $\hat{\bar{F}}_z(c)$ can be represented as a sum of a large number of random variables (e.g., 2000 samples = 200 days sampled × 10 samples per day), it is expected that the normal approximation to the sampling distribution of $\hat{\bar{F}}_z(c)$ will hold. This will allow the construction of confidence intervals for $\bar{F}_z(c)$. Thus, a 100(1-α)% confidence interval for $\bar{F}_z(c)$ is approximated by

$$\hat{\bar{F}}_z(c) \pm h_{\alpha/2}\left(\widehat{\mathrm{var}}\,\hat{\bar{F}}_z(c)\right)^{1/2} \quad ,$$

with $h_{\alpha/2}$ being the standard normal deviate defined by

$$\int_{h_{\alpha/2}}^{\infty} \frac{1}{\sqrt{2\pi}} e^{-x^2/2} dx = \alpha/2 \quad .$$

The same idea can be used to obtain 100(1-α)% upper (lower) tolerance bounds on c_ξ the level of H_2SO_4 such that $\bar{F}_z(c_\xi) = \xi$. Specifically, one finds the value $\hat{c}_{\alpha\xi}$ such that

$$\left[\hat{\bar{F}}_z(\hat{c}_{\alpha\xi}) + h_\alpha\left(\widehat{\mathrm{var}}\,\hat{\bar{F}}_z(\hat{c}_{\alpha\xi})\right)^{1/2}\right] = \xi \quad .$$

Since one is 100(1-α)% confident that $\hat{\bar{F}}(\hat{c}_{\alpha\xi}) + h_\alpha(\mathrm{var}\hat{\bar{F}})^{1/2}$ is greater than $\bar{F}(\hat{c}_{\alpha\xi})$, and since the former is equal to ξ, one is 100(1-α)% confident that $\hat{c}_{\alpha\xi} > c_\xi$.

In summary then, the sampling design is constructed to sample from a stratified set of feasible trip sequences determined by the LARTS data set. Unbiased invariant estimates are obtained for the probability that a randomly-selected trip will lead to an exposure of level c or more as a function of c. The sampling design is constructed so that error estimates may be obtained for the chosen estimators. These error estimates can be used to construct confidence bounds and tolerance intervals. The stratification procedure is made optimum by choosing the number of days each stratum is sampled appropriately. The result is that freeway trips will be taken about 12 times as often as surface street trips if the variance ratio in Eq. (3.10) is 1 to 100.

The theory upon which this sampling plan is based is presented in the next section.

FINITE POPULATION SAMPLING THEORY

Sampling from finite populations has been a recent topic in the statistical literature. Many of the important advances in this area were reviewed by Godambe [1965] and later by Solomon and Zacks [1970]. The approach described herein follows the theory and notation of Godambe [1966, 1966a, 1966b] quite closely. Because of the special considerations that must be given to this problem, certain accommodations must be made. The basic approach is a stratified sampling scheme. Solomon and Zacks [1970] quote Raj [1968] as stating, "The basic consideration involved in the formation of strata is that the strata should be internally homogeneous." If the variance within each strata is kept small, then fewer samples are required to characterize each strata. Thus, a savings in sample size and consequently data collection costs is obtained.

Consider one stratum U_{dj} with its associated set S_j of feasible sequences. Define a probability function, $p_j(s)$, on S_j. Thus

$$P_j(s) \geqslant 0 \text{ for all } s \epsilon S_j$$

and

$$\sum_{s \epsilon S_j} P_j(s) = 1 \tag{4.1}$$

will hold. Let P_{ud} be the true probability that the trip $u_d \; \epsilon \; U_{dj}$ will lead to a measured exposure of level c or more. Let $z_{udk.}$ be the average of L_{ud}

replicate measurements for the u_d'th trip taken on the dth day by the kth car. Thus

$$E\left\{I(z_{udk.} - c)\right\} = \text{Prob}\left\{z_{udk.} \geq c\right\} = p_{ud}$$

holds. That is, $I(z_{udk.} - c)$ is an unbiased estimate of p_{ud}. Since $\bar{F}_{jz}(c|d)$ is the probability that a randomly-selected trip will lead to an exposure of c or more on the dth day, we have

$$\bar{F}_{jz}(c|d) = \sum_{u \in U_{dj}} p_{ud}/N_{dj} \quad . \tag{4.2}$$

Thus, an estimate of $\bar{F}_{jz}(c|d)$ is an estimate of $\sum_{u \in U_{dj}} p_{ud}/N_{dj}$, the population average of the p_{ud}. Godambe [1955] shows that the most general linear estimator based on a sample s_k for such population averages must take the form

$$\hat{\bar{F}}_{jz}(c|d)_k = \sum_{u \in s_k} I(z_{udk.} - c)\beta(u,s_k) \quad , \tag{4.3}$$

where $\beta(u,s_k)$ are a specified set of coefficients. It is easy to show that $\hat{\bar{F}}_{jz}(c|d)_k$ will be an unbiased estimate of $\bar{F}_{jz}(c|d)$ for all possible sets of p_{ud} if and only if

$$\sum_{s \in S_j} \beta(u,s)p_j(s)\delta_{su} = 1/N_d \tag{4.4}$$

for all $u \epsilon U_{dj}$. Here δ_{su} equals zero if u is not in s and one if u is in s. Equation (4.4) is referred to as an unbiasing constraint on the $\beta(u,s)$.

Next consider the class of estimators which are invariant with respect to the function

$$f(x) = 1-x \quad .$$

That is, if we desire to estimate $F_{jz}(c|d)$ (= $1 - \bar{F}_{jz}(c|d)$) using the data $I(c - z_{udk.}) = [1 - I(z_{udk.} - c)]$, we require the estimator to satisfy

$$\hat{F}_{jz}(c|d)_k = 1 - \hat{\bar{F}}_{jz}(c|d)_k \quad .$$

This will occur if and only if

$$\sum_{u \epsilon s} \beta(u,s) = 1 \quad \text{for all} \quad s \epsilon S_j \quad . \tag{4.5}$$

Equation (4.5), interestingly, is also a necessary and sufficient requirement for the estimators to be invariant under a general location-scale shift, i.e., under all functions $f_{a,b}(x) = a + bx$.

We now seek a solution to (4.4) and (4.5) for those $\beta(u,s)$ that factor, i.e., $\beta(u,s) = \alpha(u)\beta(s)$. Though this is quite arbitrary at this point, it is nevertheless desirable to restrict our attention to a class of estimators that can be computed easily. Such a factorization restriction will result in easily calculated coefficients. (It may be of interest that all the estimators the author has encountered in the literature that are being used in practice fall into the class of estimators with factorizable coefficients.) Without loss of generality, we can assume $p(s) > 0$ for all $s \in S_j$ (if not, we simply delete those s for which $p(s) = 0$ from S_j). Write $r(s) = \beta(s)p(s)N_{dj}$ and $g(u) = 1/\alpha(u)$. Thus

$$\beta(u,s) = \frac{r(s)}{N_{dj}p(s)g(u)} \tag{4.6}$$

with g and r arbitrary to this point. From Eq. (4.4), we see that g(u) must satisfy

$$g(u) = \sum_{s \in S_j} r(s)\delta_{su} \quad \text{for each} \quad u \quad . \tag{4.7}$$

Furthermore, Eq. (4.5) implies that

$$p_j(s) = \frac{r(s)}{N_{dj}} \sum_{u \in s} \frac{1}{g(u)} \tag{4.8}$$

must hold. Writing $g(u) = g_u$, we see that

$$\beta(u,s) = \frac{1/g_u}{\sum_{u \in s} 1/g_u} \quad . \tag{4.9}$$

Equations (4.7), (4.8), and (4.9) give the most general solution to (4.4) and (4.5) for $\beta(u,s) = \alpha(u)\beta(s)$. The values of r(s) in (4.7) and (4.8) are completely arbitrary. Note if $r(s) = 1$ for all s, then g(u) equals the number of sequences that contain the trip u. This is the solution that was chosen in Section 3.

Some thought has been given to choosing an optimum set of r(s). It is possible to generate a group of à priori estimates of the p_{ud}. Such estimates can be used to obtain an à priori estimate of the variance of $\hat{\bar{F}}_{jz}(c|d)_k$. It is then reasonable to choose the r(s) to minimize this variance. Unfortunately, the algebra gets quite involved. The number of unknowns makes the problem difficult even on present-day computing equipment. Unless a shortcut is found, the effort does not seem worthwhile. More work may yet be done in this area.

With the above notation, the estimator for the sample s_k now takes the form

$$\hat{\bar{F}}_{jz}(c|d)_k = \left(\sum_{u\varepsilon s_k} I(z_{udk.} - c)/g_u\right)\Big/\sum_{u\varepsilon s} 1/g_u \quad , \tag{4.10}$$

which is just a weighted average of the $I(z_{udk.} - c)$. The variance of the general linear unbiased estimator given in (4.3) is

$$\begin{aligned} \mathrm{var}\left(\hat{\bar{F}}_{jz}(c|d)_k\right) &= E\left\{\left(\hat{\bar{F}}_{jz}(c|d)_k - \bar{F}_{jz}(c|d)\right)^2\right\} \\ &= \sum_{s_k\varepsilon S_j} p(s) \sum_{u\varepsilon s_k} p_{ud}(1 - p_{ud})\beta^2(u,s_k) + \sum_{s} p(s) \left(\sum_{u\varepsilon s_k} p_{ud}\beta(k,s_k)\right)^2 \\ &\quad - \bar{F}^2_{jz}(c|d) \quad . \end{aligned} \tag{4.11}$$

If one considers sampling K_{dj} times from S_j on the dth day, an overall estimate for the day can be written

$$\begin{aligned}\hat{\bar{F}}_{jz}(c|d) &= \sum_{k=1}^{K_{dj}} \frac{1}{K_{dj}} \left(\sum_{u\varepsilon s_k} I(z_{udk.} - c)/g_u\right) \Big/ \left(\sum_{u\varepsilon s_k} 1/g_u\right) \\ &= \sum_{k=1}^{K_{dj}} \frac{1}{K_{dj}} \hat{\bar{F}}_{jz}(c|d)_k \quad . \end{aligned} \tag{4.12}$$

Independent sampling of sequences from S_j implies

$$\begin{aligned}\mathrm{var}\left(\hat{\bar{F}}_{jz}(c|d)\right) &= \frac{1}{K_{dj}} \mathrm{var}\left(\hat{\bar{F}}_{jz}(c|d)_k\right) \\ &= \frac{1}{K_{dj}} \left\{ \sum_{s\varepsilon S_j} p_j(s) \left(\sum_{u\varepsilon s} p_{ud}(1 - p_{ud})\beta^2(u,s) \right) \right. \\ &\quad \left. + \sum_{s\varepsilon S_j} p_j(s) \left(\sum_{u\varepsilon s} p_{ud}\beta(u,s) \right)^2 - \bar{F}^2_{jz}(c|d) \right\} \quad . \end{aligned} \tag{4.13}$$

For $\beta(u,s)$ and $p(s)$ given by (4.6) and (4.8), we have

$$\begin{aligned}\mathrm{var}\left(\hat{\bar{F}}_{jz}(c|d)\right) &= \frac{1}{K_{dj}} \left[\sum_{s\varepsilon S_j} \frac{r_s}{N_{dj} \sum_{u'} \frac{\delta_{su'}}{g_{u'}}} \sum_u \frac{p_{ud}(1 - p_{ud})\delta_{su}}{g_u^2} \right. \\ &\quad \left. + \sum_s \frac{r_s}{N_{dj} \sum \frac{\delta_{su'}}{g_{u'}}} \left(\sum_u \frac{p_{ud}\delta_{su}}{g_u} \right)^2 - \bar{F}^2_{jz}(c|d) \right] \quad , \end{aligned} \tag{4.14}$$

with g_u given by (4.7).

It now remains to show how the estimates $\hat{\bar{F}}_{jz}(c|d)$ for each stratum and each day are combined to provide an estimate of $\bar{F}_z(c)$ the overall probability that a randomly-selected trip taken sometime in D will lead to an exposure of c or more. If N_j is the number of trips in D for stratum j, and $\lambda_j = N_j / \sum_{j=1}^{J} N_j$, J being the number of strata, then

$$\bar{F}_z(c) = \sum_{j=1}^{J} \lambda_j \bar{F}_{jz}(c) \quad . \tag{4.15}$$

Since each trip is to be considered equally likely in the definition of $\bar{F}_{jz}(c)$, we have

$$\bar{F}_{jz}(c) = \sum_{d \in D} \frac{N_{dj}}{N_j} \bar{F}_{jz}(c|d) \quad . \tag{4.16}$$

Each N_{dj} represents the total number of trips taken in Los Angeles within the jth stratum on the dth day. Undoubtedly, these will vary from day to day. However, if the LARTS data set is used to define the U_d, this will not be the case. Nevertheless, corrections for total number of trips can be made if estimates of these are available. For the remainder, we will proceed as though such estimates exist (e.g., from CALTRANS data sources). That is, we have a function $\hat{w}_j(d)$ such that

$$E\left(\hat{w}_j(d)\right) = w_j(d) \equiv N_{dj}/N_j \quad . \tag{4.17}$$

We will require these estimates to be independent of the $\hat{\bar{F}}_{jz}(c|d)$. In order to combine the $\hat{\bar{F}}_{jz}(c|d)$ properly, we need to know the probability $h(q_j)$ of obtaining the sample days $q_j = (d_1, \ldots, d_{m_j})$ from D. For ease of implementation assume this is done using simple random sampling without replacement. Thus

$$h(q_j) = \frac{1}{\binom{M}{m_j}} \quad , \tag{4.18}$$

where M is the total number of days in D and m_j is the total number of days in q_j. Here, m_j is considered fixed.

With this sampling design we have that

$$\hat{\bar{F}}_{jz}(c) = \frac{M}{m_j} \sum_{d \epsilon q_j} \hat{\bar{F}}_{jz}(c|d)\hat{w}_j(d) \quad , \tag{4.19}$$

with $\hat{\bar{F}}_{jz}(c|d)$ given by (4.12), is an unbiased estimate of $\bar{F}_{jz}(c)$. The $\hat{\bar{F}}_{jz}(c)$ are combined in the obvious manner to obtain an estimate of $\bar{F}_z(c)$. Thus

$$\hat{\bar{F}}_z(c) = \sum_{j=1}^{J} \lambda_j \hat{\bar{F}}_{jz}(c) \tag{4.20}$$

In order to obtain the appropriate expressions for the variance of this estimator, it is necessary at this point to become specific concerning the nature of the stratified sampling procedure. We have the constraint that on any day d we can send out at most K pairs of cars. These pairs will be allocated to the J strata according to the allocation $t_i = (K_{i1}, \ldots, K_{iJ})$. That is, the ith allocation, t_i, sends K_{ij} pairs of cars into stratum j. Maximum use of the vehicles at hand implies

$$\sum_{j=1}^{J} K_{ij} = K \tag{4.21}$$

for each allocation t_i.

Define v_i as the number of days allocation type t_i is to be used. If there are R allocation types, then

$$\sum_{i=1}^{R} v_i = m \quad , \tag{4.22}$$

where m is the number of days sampled from the set D of M days. For now, consider the $v_1,\ldots,v_R$ fixed. In Section 4.1 we will demonstrate how they should be chosen so as to minimize the variance of $\hat{F}_Z(c)$. The stratified plan is to choose the set of days, q, of size m from D using simple random sampling without replacement. Once the set q is chosen, the allocations t_i are distributed among these m days completely randomly with probability $\prod_{i=1}^{R} v_i!/m!$. Let q_i be the set of days in q which uses allocation type t_i. The above procedure implies the probability of observing any q_i is

$$h(q_i) = \frac{1}{\binom{M}{v_i}} \quad . \tag{4.23}$$

We have defined m_j as the number of days stratum j is sampled. Clearly

$$m_j = \sum_{i \mid t_i \ni j} v_i \quad , \tag{4.24}$$

where the notation $i \mid t_i \ni j$ refers to summation over all indexes i such that allocation t_i sends at least one pair of cars to stratum j ($K_{ij} > 0$).

Let $m_{jj'}$ be the number of days both stratum j and j′ are sampled simultaneously. Thus

$$m_{jj'} = \sum_{i \mid t_i \ni j,j'} v_i \quad , \tag{4.25}$$

where now the sum ranges over all i such that K_{ij} and $K_{ij'}$ are both greater than zero.

Because of the nature of the sampling procedure, the probability distributions for q_j, the set of days stratum j is sampled, and $q_{jj'}$, the set of days both j and j' are sampled, are

$$h(q_j) = \frac{1}{\binom{M}{m_j}} \tag{4.26}$$

and

$$h(q_{jj'}) = \frac{1}{\binom{M}{m_{jj'}}} \tag{4.27}$$

respectively. With these results, we are now able to construct the expression for the variance of $\hat{\hat{F}}_z(c)$.

From (4.20), we see that

$$\mathrm{var}\left(\hat{\hat{F}}_z(c)\right) = \sum_{j=1}^{J} \lambda_j^2 \mathrm{var}\left(\hat{\hat{F}}_{jz}(c)\right) + \sum_{j \neq j'}\sum \lambda_j \lambda_{j'} \mathrm{cov}\left(\hat{\hat{F}}_{jz}(c), \hat{\hat{F}}_{j'z}(c)\right) \tag{4.28}$$

Note that, contrary to the usual stratified sampling applications, e.g., Bennett and Franklin [1954], the covariance between $\hat{\hat{F}}_{jz}(c)$ and $\hat{\hat{F}}_{j'z}(c)$ is not necessarily zero. This is because we are constrained to having only K cars on any given day. Thus we cannot sample completely independently from stratum j and stratum j′. The covariances in (4.28) are a function of the true covariance between the $\bar{\bar{F}}_{jz}(c|d)$ and $\bar{\bar{F}}_{j'z}(c|d)$. First, however, let us consider the variance terms in (4.28).

Since $\hat{\bar{\bar{F}}}_{jz}(c)$ is an unbiased estimator of $\bar{\bar{F}}_{jz}(c)$, we have

$$\operatorname{var}\left(\hat{\bar{\bar{F}}}_{jz}(c)\right) = E\left\{\left(\hat{\bar{\bar{F}}}_{jz}(c) - \bar{\bar{F}}_{jz}(c)\right)^2\right\} \quad . \tag{4.29}$$

Suppressing the variables z and c and writing $\bar{\bar{F}}_{jz}(c|d) = \bar{\bar{F}}_{jd}$, $\hat{\bar{\bar{F}}}_{jz}(c|d) = \hat{\bar{\bar{F}}}_{jd}$, etc., we have

$$\begin{aligned} \operatorname{var}(\hat{\bar{\bar{F}}}_j) &= E\left\{(\hat{\bar{\bar{F}}}_j - \bar{\bar{F}}_j)^2\right\} \\ &= E(\hat{\bar{\bar{F}}}{}_j^2) - \bar{\bar{F}}{}_j^2 \\ &= \sum_{q_j} h(q_j) E_{|q_j}\left\{\left(\sum_{d \varepsilon q_j} (M\hat{w}_{jd})\hat{\bar{\bar{F}}}_{jd}\right)^2 \Big/ m_j^2\right\} - \bar{\bar{F}}{}_j^2 \quad . \end{aligned} \tag{4.30}$$

The inner expectation is taken for fixed q_j. The outer sum is over all possible subsets, q_j of size m_j in D. Note that if N_{dj} is constant, then $N_j = \sum_d N_{dj} = MN_{dj}$. Thus, $w_{jd}M$ would equal one. In any case, after much algebra, one finds

$$\operatorname{var}(\hat{\bar{F}}_j) = \left(\sum_{d\varepsilon D} (Mw_{jd})^2 + \operatorname{var}(M\hat{w}_{jd})\operatorname{var}(\hat{\bar{\bar{F}}}_{jdk})\right)\Big/ M$$

$$\cdot \left(\sum_{i=1 | t_i \ni j} v_i / K_{ij}\right)\Big/ m_j^2$$

$$+ \left(\sum_{d\varepsilon D} \bar{F}_{jd}^2 \operatorname{var}(M\hat{w}_{jd})/M\right)\Big/ m_j$$

$$+ \frac{1}{m_j}\left(1 - \frac{m_j}{M}\right)\left(\frac{1}{M-T}\right)\cdot \sum_{d\varepsilon D} (\bar{F}_{jd} - \bar{F}_j)^2 \quad . \tag{4.31}$$

In the above, the variance of $\hat{\bar{\bar{F}}}_{jdk}$ is given by Eq. (4.11). Thus,

$$\operatorname{var}(\hat{\bar{\bar{F}}}_{jdk}) = E(\hat{\bar{\bar{F}}}_{jdk} - \bar{F}_{jd})^2$$

$$= \sum_{s_k \varepsilon S_j} p_j(s) \sum_{u\varepsilon s_k} p_{ud}(1-p_{ud})\beta^2(u,s_k) + \sum_{s_k} p_j(s_k)\left(\sum_{u\varepsilon s_k} p_{ud}\beta(u,s_k)\right)^2$$

$$- \bar{\bar{F}}_{jd}^2 \quad . \tag{4.32}$$

The $\beta(u,s_k)$ in the above are any set of coefficients satisfying the unbiasing constraint (4.4). In particular, those given by (4.6) through (4.9) are valid. Note this variance is not a function of k, but is a function of d through the p_{ud}.

In order to complete the computation of the variance of $\hat{\bar{F}}_z(c)$ from Eq. (4.28), we need the covariance between $\hat{\bar{F}}_j$ and $\hat{\bar{F}}_{j'}$. Straightforward calculations reveal that

$$\operatorname{cov}(\hat{\bar{F}}_j,\hat{\bar{F}}_j)_y = \frac{Mm_{jj'} - m_j m_{j'}}{m_j m_{j'}(M-1)} \frac{1}{M} \sum_{d\varepsilon D} (Mw_{jd}\bar{F}_{jd} - \bar{F}_j)$$

$$\cdot\ (Mw_{j'd}\bar{F}_{j'd} - \bar{F}_{j'})$$

$$+ \frac{m_{jj'}}{m_j m_{j'}} \frac{1}{M} \sum_{d\varepsilon D} \bar{F}_{jd}\bar{F}_{j'd}\operatorname{cov}(M\hat{w}_{jd},M\hat{w}_{j'd}|d) \quad , \qquad (4.33)$$

where $\operatorname{cov}(M\hat{w}_{jd},M\hat{w}_{j'd}|d)$ is the covariance between $M\hat{w}_{jd}$ and $M\hat{w}_{j'd}$ for the dth day. This term is non-zero because of the constraint $\sum_{j=1}^{J} \hat{w}_{jd} = 1$.

Equations (4.31), (4.32), and (4.33) allow one to compute the variance of $\hat{\bar{F}}_z(c)$ given by Eq. (4.28). This formulation assumes the $\lambda_j(N_j/\sum_{j=1}^{J} N_j)$ are known. They can be estimated with a fair degree of precision from the LARTS data set. For the procedure set forth in Section 2, λ_1 equals the ratio of number of surface street trips to total trips for the set D and λ_2 equals $1-\lambda_1$.

The variance expression for $\hat{\bar{F}}_z(c)$ becomes useful if one has a procedure to estimate it. Below we present a scheme which estimates this variance unbiasedly. In order to do this, we must either assume $M\hat{w}_{jd} = 1$ for all d or that we have an unbiased estimate of the variance of $M\hat{w}_{jd}$. Let the latter more general case hold. Call the estimate of this variance $\widehat{\operatorname{var}}(M\hat{w}_{jd})$. We can then develop the following equalities. First let

$$\hat{A}_1 = \left\{\sum_{d\varepsilon q_j}\left(\hat{\bar{F}}^2_{jd} - \sum_{k=1}^{k_{dj}} (\hat{\bar{F}}_{jdk} - \hat{\bar{F}}_{jd})^2/[K_{dj}(K_{dj} - 1)]\right)\widehat{\operatorname{var}}(M\hat{w}_{jd})\right\}\Big/ m_j \qquad (4.34)$$

$$\hat{A}_2 = \left\{ \sum_{d \varepsilon q_j} \sum_{k=1}^{K_{dj}} (M\hat{w}_{jd})^2 \frac{(\hat{\bar{\bar{F}}}_{jdk} - \hat{\bar{\bar{F}}}_{jd})^2}{K_{dj} - 1} \right\} \Big/ m_j \quad , \tag{4.35}$$

and

$$\hat{A}_3 = \sum_{d \varepsilon q_j} (\hat{\bar{\bar{F}}}_{jd} M\hat{w}_{jd} - \hat{\bar{\bar{F}}}_j)^2 / (m_j - 1) \quad . \tag{4.36}$$

It can then be shown that

$$E(\hat{A}_1) = \frac{1}{M} \sum_{d \varepsilon D} \bar{\bar{F}}_{jd}^2 \operatorname{var}(M\hat{w}_{jd}) \quad , \tag{4.37}$$

$$E(\hat{A}_2) = \frac{1}{M} \sum_{d \varepsilon D} \left((Mw_{jd})^2 + \operatorname{var}(M\hat{w}_{jd}) \right) \operatorname{var} \hat{\bar{\bar{F}}}_{jdk} \quad , \tag{4.38}$$

and

$$\begin{aligned} E(\hat{A}_3) = {} & \left(\sum_{d \varepsilon D} \left((Mw_{jd})^2 + \operatorname{var}(M\hat{w}_{jd}) \right) \operatorname{var} \hat{\bar{\bar{F}}}_{jdk} / M \right) \\ & \cdot \left(\sum_{i=1/t_i \ni j}^{R} v_i / K_{ij} \right) \Big/ m_j + \sum_{d \varepsilon D} \bar{\bar{F}}_{jd}^2 \operatorname{var}(M\hat{w}_{jd}) / M \\ & + \frac{1}{M-1} \sum_{d \varepsilon D} (Mw_{jd} \bar{\bar{F}}_{jd} - \bar{\bar{F}}_j)^2 \quad . \end{aligned} \tag{4.39}$$

Calling the unbiased estimate of the variance of $\hat{\bar{\bar{F}}}_j$ $\widehat{\operatorname{var}}(\hat{\bar{\bar{F}}}_j)$, we see that

$$\widehat{var}(\hat{F}_j) = \hat{A}_1/M + \hat{A}_2 \left(\sum_{i=1 | t_i \ni j}^{R} v_i/K_{ij} \right) \cdot \frac{1}{m_j M} + \hat{A}_3 \frac{1}{m_j} \left(1 - \frac{m_j}{M} \right) \qquad (4.40)$$

has the proper expectation.

An unbiased estimate of the covariance between $\hat{F}_j$ and $\hat{F}_{j'}$ can be developed in an analogous manner. To do this, however, we need an unbiased estimate of the covariance between $M\hat{w}_{jd}$ and $M\hat{w}_{j'd}$. Call such an estimate $\widehat{cov}(M\hat{w}_{jd}, M\hat{w}_{j'd})$. For the case J = 2, this can be taken equal to the negative of the variance of either $M\hat{w}_{1d}$ or $M\hat{w}_{2d}$, which are equal for J = 2. To see this, just note that $\hat{w}_{1d} + \hat{w}_{2d} = 1$ implies $E(\hat{w}_{1d}, \hat{w}_{2d})$ equals $w_{1d}w_{2d} - var(\hat{w}_{1d})$ and $var(\hat{w}_{1d}) = var(\hat{w}_{2d})$. Thus, for J = 2, $\widehat{cov}(M\hat{w}_{jd}, M\hat{w}_{j'd}) = -\widehat{var}(M\hat{w}_{2d})$.

The estimate of the covariance between $\hat{F}_j$ and $\hat{F}_{j'}$ is obtained from the expressions

$$\hat{B}_1 = \frac{1}{m_{jj'} - 1} \sum_{d \epsilon q_{jj'}} (M\hat{w}_{jd}\hat{F}_{jd} - \hat{\hat{F}}{}^*_j)(Mw_{j'd}\hat{F}_{j'd} - \hat{\hat{F}}{}^*_{j'}) \qquad (4.41)$$

and

$$\hat{B}_2 = \frac{1}{m_{jj'}} \sum_{d \epsilon q_{jj'}} \hat{F}_{jd}\hat{F}_{j'd}\widehat{cov}(M\hat{w}_{jd}, M\hat{w}_{j'd}) \quad . \qquad (4.42)$$

In (4.36) $\hat{\hat{F}}{}^*_j$ is given by

$$\hat{\hat{F}}{}^*_j = \sum_{d \epsilon q_{jj'}} M\hat{w}_{jd}\hat{F}_{jd}/m_{jj'} \quad . \qquad (4.43)$$

That is, the $\hat{\bar{F}}_j^*$ only contain data from days in $q_{jj'}$, the set of days for which both stratum j and stratum j' are sampled. It is an easy matter to show that

$$E(\hat{B}_1) = \frac{1}{M-1} \sum_{d\epsilon D} (\bar{F}_{jd} Mw_{jd} - \bar{F}_j)(\bar{F}_{j'd} Mw_{j'd} - \bar{F}_{j'})$$

$$+ \frac{1}{M} \sum_{d\epsilon D} \bar{F}_{jd} \bar{F}_{j'd} \operatorname{cov}(M\hat{w}_{jd}, M\hat{w}_{j'd} | d) \tag{4.44}$$

and

$$E(\hat{B}_2) = \frac{1}{M} \sum_{d\epsilon D} \bar{F}_{jd} \bar{F}_{j'd} \operatorname{cov}(M\hat{w}_{jd}, M\hat{w}_{j'd} | d) \quad . \tag{4.45}$$

Thus, an unbiased estimate of $\operatorname{cov}(\hat{\bar{F}}_j, \hat{\bar{F}}_{j'})$ is

$$\widehat{\operatorname{cov}}(\hat{\bar{F}}_j, \hat{\bar{F}}_{j'}) = \frac{Mm_{jj'} - m_j m_{j'}}{Mm_j m_{j'}} \hat{B}_1 + \hat{B}_2/M \quad . \tag{4.46}$$

The estimates given by Eqs. (4.40) and (4.46) can be used in Eq. (4.28) to obtain an estimate of the variance of $\hat{\bar{F}}_z(c)$. Thus

$$\widehat{\operatorname{var}}\left(\hat{\bar{F}}_z(c)\right) = \sum_{j=1}^{J} \lambda_j^2 \widehat{\operatorname{var}}\left(\hat{\bar{F}}_{jz}(c)\right) + \sum_{j \neq j'}\sum \lambda_j \lambda_{j'} \widehat{\operatorname{cov}}\left(\hat{\bar{F}}_{jz}(c), \hat{\bar{F}}_{j'z}(c)\right) \quad . \tag{4.47}$$

The estimator $\hat{\bar{F}}_z(c)$ can be written as a linear combination of a great number of independent samples. It is expected that this number will be large enough for the *Central Limit Theorem* to apply. If this is so, then the sampling distribution of $\hat{\bar{F}}_z(c)$ will be approximately normal. In such a case, confidence intervals and tolerance intervals are easily obtained. Let h_α be an upper αth percentage point of the standard normal distribution. That is

$$\int_{h_\alpha}^{\infty} \frac{1}{\sqrt{2\pi}} e^{-x^2/2} dx = \alpha \quad . \tag{4.48}$$

Then an approximate $100(1-\alpha)\%$ confidence interval for $\bar{F}_z(c)$ for each c is

$$\hat{\bar{F}}_z(c) \pm h_{\alpha/2}\left[\widehat{\text{var}}\left(\hat{\bar{F}}_z(c)\right)\right]^{1/2} \quad . \tag{4.49}$$

A $100(1-\alpha)\%$ upper tolerance bound on c_ξ, the $(1-\xi)$th percentile of $F_z(c)$, is given by solving

$$\hat{\bar{F}}(\hat{c}_{\alpha\xi}) + h_\alpha\left[\widehat{\text{var}}\left(\hat{\bar{F}}_z(\hat{c}_{\alpha\xi})\right)\right]^{1/2} = \xi \tag{4.50}$$

for $\hat{c}_{\alpha\xi}$. This is so since

$$1-\alpha = P\left\{\hat{\bar{F}}_z(c) + h_\alpha\left[\widehat{\text{var}}\left(\hat{\bar{F}}_z(c)\right)\right]^{1/2} > \bar{F}_z(c)\right\} \tag{4.51}$$

holds for each c. In particular, for $c = \hat{c}_{\alpha\xi}$ in (4.50),

$$1-\alpha = P\left\{\hat{\bar{F}}_Z(\hat{c}_{\alpha\xi}) + h_\alpha\left(\widehat{\mathrm{var}}\hat{\bar{F}}(\hat{c}_{\alpha\xi})\right)^{1/2} \geq \bar{F}(\hat{c}_{\alpha\xi})\right.$$

$$= P\left\{\xi \geq \bar{F}(\hat{c}_{\alpha\xi})\right\}$$

$$= P\left\{\bar{F}^{-1}(\xi) \leq F^{-1}\bar{F}(\hat{c}_{\alpha\xi})\right\}$$

$$= P\left\{c_\xi \leq \hat{c}_{\alpha\xi}\right\} \quad . \qquad (4.52)$$

A lower 100(1-α)% tolerance bound for c_ξ is obtained by reversing the sign in Eq. (4.50).

4.1 Stratification Optimization

In this section, we address the problem of how to choose the number of days v_i each allocation type t_i should be used. The set $(v_1,\ldots,v_R)$ will be chosen so as to minimize the variance of $\hat{F}_Z(c)$ as given by Eq. (4.28) in conjunction with Eqs. (4.31), (4.32), and (4.33). We consider the total number of days sampled to be fixed. Then, the v_i must satisfy the constraint

$$\sum_{i=1}^{R} v_i = m \quad . \qquad (4.1.1)$$

Using the method of Lagrange multipliers, we seek the unconstrained minimum of

$$H = \sum \lambda_j^2 \mathrm{var}(\hat{F}_j) + \sum_{j}\sum_{\neq j'} \lambda_j\lambda_{j'}\mathrm{cov}(\hat{F}_j,\hat{F}_{j'}) + \mu\left(\sum_{i=1}^{R} v_i - m\right) \qquad (4.1.2)$$

with respect to the parameters $v_1,\ldots,v_R,\mu$. Differentiating with respect to the v_i, we have

$$\frac{\partial H}{\partial v_i} = \sum_j \lambda_j^2 \frac{\partial \mathrm{var}(\hat{\bar{F}}_j)}{\partial v_i} + \sum_{j}\sum_{\neq j'} \frac{\partial \mathrm{cov}(\hat{\bar{F}}_j, \hat{\bar{F}}_{j'})}{\partial v_i} + \mu \quad . \tag{4.1.3}$$

From the definitions of m_j and $m_{jj'}$, we see that

$$\frac{\partial m_j}{\partial v_i} = \delta_{t_i j} \tag{4.1.4}$$

$$\frac{\partial m_{jj'}}{\partial v_i} = \delta_{t_i j}\delta_{t_i j'} \quad , \tag{4.1.5}$$

where $\delta_{t_i j}$ is zero if $K_{ij} = 0$ and one if $K_{ij} > 0$. Let

$$\overline{\sigma^2_{j1}} = \mathrm{ave}\left\{\left((Mw_{jd})^2 + \mathrm{var}\left(M\hat{w}_{jd}\right)\right) \mathrm{var}\hat{\bar{F}}_{jdk}\right\} \tag{4.1.6}$$

$$\overline{\sigma^2_{j2}} = \mathrm{ave}\left\{\bar{F}^2_{jd}\mathrm{var}(M\hat{w}_{jd})\right\} \tag{4.1.7}$$

$$\overline{\sigma^2_{j3}} = \mathrm{ave}\left\{(\bar{F}_{jd} - \bar{F}_j)^2\right\} \quad , \tag{4.1.8}$$

where the averaging operators are with respect to days in D. Similarly, let

$$\overline{\sigma^2_{jj'1}} = \mathrm{ave}\left\{(Mw_{jd}\bar{F}_{jd} - \bar{F}_j)(Mw_{j'd}\bar{F}_{j'd} - \bar{F}_{j'})\right\} \tag{4.1.9}$$

$$\overline{\sigma^2_{jj'2}} = \text{ave}\left\{\bar{F}_{jd}\bar{F}_{j'd}\,\text{cov}(M\hat{w}_{jd}, M\hat{w}_{j'd})\right\} \quad . \tag{4.1.10}$$

We will optimize for the case when M is very large. Then, from (4.31) and (4.33), we see that as M → ∞,

$$\text{var}(\hat{\bar{F}}_j) = \frac{1}{m_j}\left\{\overline{\sigma^2_{j1}}\left(\sum_{i=1|t_i\ni j}^{R} v_i/K_{ij}\right)\Big/m_j + \overline{\sigma^2_{j2}} + \overline{\sigma^2_{j3}}\right\} \tag{4.1.11}$$

and

$$\text{cov}(\hat{\bar{F}}_j, \hat{\bar{F}}_{j'}) = \frac{m_{jj'}}{m_j m_{j'}}\left[\overline{\sigma^2_{jj'1}} + \overline{\sigma^2_{jj'2}}\right] \tag{4.1.12}$$

Since the variance and covariance terms given in (4.1.6) through (4.1.9) are not a function of the v_i, we see from (4.1.3) through (4.1.5) and (4.1.10) and (4.1.12) that for M large

$$\begin{aligned}\frac{\partial H}{\partial v_i} = \sum_{j=1}^{J} \lambda_j^2 \Bigg\{ &- \frac{\delta_{t_i j}}{m_j^2}\left(\overline{\sigma^2_{j1}}\left(\sum_{i'=1|t_{i'}\ni j}^{R} v_{i'}/K_{i'j}\right)\Big/m_j + \overline{\sigma^2_{j2}} + \overline{\sigma^2_{j3}}\right) \\ &+ \frac{1}{m_j}\left[\sigma^2_{j1}\left(\frac{\delta_{t_i j}}{K_{ij}m_j} - \left(\sum_{i'=1|t_{i'}\ni j}^{R} v_{i'}/K_{i'j}\right)\frac{\delta_{t_i j}}{m_j^2}\right)\right]\Bigg\} \\ &+ \sum_{j}\sum_{\neq j'} \lambda_j\lambda_{j'}\left(\overline{\sigma^2_{jj'1}} + \overline{\sigma^2_{jj'2}}\right)\left\{\frac{\delta_{t_i j}\delta_{t_i j'}}{m_j m_{j'}} - \frac{m_{jj'}\delta_{t_i j}}{m_j^2 m_{j'}} \right. \\ &\left. - \frac{m_{jj'}\delta_{t_i j'}}{m_j m_{j'}^2}\right\} + \mu\end{aligned} \tag{4.1.13}$$

To determine the v_i, the right-hand side of (4.1.13) is set equal to zero for each i. The resulting system of equations is then solved for the v_i in terms of the λ_j and variance and covariance terms. One must have à priori estimates of these terms in order for this procedure to be useful. The best way to obtain such estimates is to run a small sample study prior to the implementation of the full experimental program. Data from this preliminary study can be used to estimate the necessary variance and covariance terms.

In the above, no consideration is given to the desire that one will want to be able to estimate the variances of $\hat{\bar{F}}_z(c)$ after the data are taken. This would be done using (4.47). From (4.34) and (4.35), it is seen that each day will provide information to estimate the variance within the jth stratum only if at least two cars are sent into that stratum on that day. Furthermore, an estimate of the covariance is possible if $m_{jj'}$ is at least 2. For our case, the only strata being considered are surface street trips and freeway trips. Because we are fairly sure that the freeway trips will yield the highest exposure levels and thus represent the highest health hazard, it is desirable to measure this effect each day that is being sampled. To this end, it is reasonable to restrict attention to the two allocations $t_1 = (0,4)$ and $t_2 = (2,2)$. That is, either all four pairs of cars will be sent on the freeways or two pairs will go on the freeways and two pairs will go on the surface streets. Such a design emphasizes the freeway system but also allows all the variances and covariances to be estimated. If m is the number of days sampled, then the above allocation implies

$$m_1 = v_2$$

$$m_2 = m$$

$$m_{12} = v_2$$

$$v_1 = m - v_2 \quad .$$

For this restricted allocation, the solution is

$$\frac{v_2}{m} = \frac{\lambda_1}{\lambda_2} \left[\frac{\overline{\sigma^2_{11}}/2 + \overline{\sigma^2_{12}} + \overline{\sigma^2_{13}}}{\overline{\sigma^2_{21}}/4} \right]^{1/2} \tag{4.1.14}$$

$$v_1 = m - v_2 \tag{4.1.15}$$

Note, the dependence on the covariance terms $\sigma^2_{jj'1}$ and $\sigma^2_{jj'2}$ has been eliminated.

USE OF THE LARTS DATA SET IN THE EXPERIMENTAL PROGRAM

In order to implement the sampling design that has been proposed, it is necessary to be able to sample from the population of trips under consideration. The presence of a rather extensive data bank collected for the Los Angeles Regional Transit Study (LARTS [1971] report) facilitates this task for the Los Angeles area. These data include trip information (origin, destination, purpose, etc.) derived from a survey of over 30,000 households in 1967 as well as on-road surveys that year. The data base will be updated shortly to include information gathered in 1976. Information on over 300,000 trips exists in the data set. A study was performed by the LARTS group at CALTRANS, the California Transit Authority, to verify the representativeness of the LARTS data set. It was determined that inferences on the total population of trips in the Los Angeles area might be off by as much as 7% if these inferences are based on the LARTS data only. The major reasons proposed for these discrepancies are that the households surveyed either forgot trips they took on the days they were being sampled or they simply neglected to record them because they felt they were unimportant. Initially, no attempt was made to adjust the data set to account for these factors.

In our application, we are not interested in the total number of trips per se. What is important is that the mix of trips be as representative as possible. This would occur if the trips that were not recorded in the LARTS survey occurred randomly, without preference to trip type and location. A certain amount of checks were made along these lines in the 1967 LARTS study. It was found that the trip volume estimated for various subsections within

Los Angeles might be off as much as 30% for certain areas, the worst area being Inglewood-Gardena. These checks were considered less reliable, however, because of the method used to assign routes to the surveyed trips.

Comparisons were made between the freeway miles traveled in the LARTS data and independent estimates from the National Highway Functional Classification Study. The differences ranged from 5% to 35% for differing freeways. This magnitude of variability indicates the difficulty in obtaining highly reliable traffic information. Nevertheless, the traffic information is essential in order to relate the concentrations of H_2SO_4 on the highway network to health effects on the community. The costs, however, of obtaining more reliable data appear prohibitive.

CALTRANS has conducted a study which allows certain adjustments to be made to the LARTS data set to make it more representative of the true trip population. For example, it was found that the LARTS data set indicates the number of trips originating from certain zones ought to be increased by factors depending on those zones. This can be made more general by supposing there is such a factor for each trip, u. Call this factor a_{ud}, for the dth day. Then the probability of exceeding on the given day is

$$\bar{F}_z(c|d) = \sum_{u=1}^{N} a_{ud} p_{ud} \Big/ \sum_{u=1}^{N} a_{ud} \quad . \tag{5.1}$$

The theory discussed in Section 4 is just as applicable to estimating (5.1) as it is to the unweighted sum of the p_{ud}. If we rewrite (5.1) as

$$\hat{F}_z(c|d) = \sum_{u=1}^{N} a'_{ud} p_{ud}/N \quad , \tag{5.2}$$

with

$$a'_{ud} = a_{ud}/\bar{a} \tag{5.3}$$

and

$$\bar{a} = \sum_{u=1}^{N} a_{ud}/N \quad , \tag{5.4}$$

and consider factored coefficient $\beta(u,s)$ of the form

$$\beta(u,s) = \frac{a'_u r_s}{Np(s)\alpha_u} \quad , \tag{5.5}$$

we see that, to obtain unbiased, invariant estimators, the α_u and $p(s)$ must satisfy

$$\alpha_u = \sum_s r_s \delta_{su} \tag{5.6}$$

$$p(s) = \frac{r_s}{N} \sum_{u \in s} a'_{ud}/\alpha_u \quad , \tag{5.7}$$

with r_s arbitrary.

The above imply that the estimator $\hat{F}_z(c|d)$ will take the form

$$\hat{F}_z(c|d) = \left[\sum_{u\in s} a'_{ud} I(z_{ud.} - c)/\alpha_u\right] \Big/ \left(\sum_{u\in s} a'_{ud}/\alpha_u\right) \tag{5.8}$$

The stratification procedure would proceed the same as in Section 4.

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TYPING GUIDE SHEET

NOMENCLATURE

c:	an arbitrarily specified level of H_2SO_4 exposure for which the probability of exceeding is to be determined
c_ξ:	the level of exposure for which the probability is ξ that a randomly-selected trip will lead to an exposure of c_ξ or more
t:	time
Θ:	the time defined for health effects purposes over which average exposure is to be determined
T:	trip length in time
$[H_2SO_4]_{back}$:	H_2SO_4 concentration off freeway and major surface streets
$[H_2SO_4]_t$:	concentration of H_2SO_4 as a function of time along a trip path
y:	maximum Θ-minute average exposure for a given trip
z_{ud}:	measured approximation to maximum Θ-minute average exposure for a given trip u on the dth day
u:	index indicating the uth trip in a set of trips under consideration
s_k;s:	sequence of trips $(u_1,\ldots,u_{n_s})$
n_s:	sample size for the sequence, s

$\bar{F}_y(c)$:	probability that a randomly-selected trip will lead to a maximum -minute exposure of c or more. (The bar above F indicates the complement of $F_y(c)$, the probability that a randomly-selected trip will lead to an exposure less than c.)
$\bar{F}_z(c)$:	the probability that a randomly-selected trip will lead to a measured exposure of c or more
N_d:	number of trips in the set U_d
U_d:	the population of trips about which inferences are to be made for the dth day (e.g., all trips in Los Angeles County originating between 6 a.m. and 11 a.m.)
D:	the set of days, d, about which inferences are to be made
d:	the dth day in D
N_T:	the total number of trips over all days, $N_T = \sum_{d \varepsilon D} N_d$
$\bar{F}_z(c\|d)$:	the probability a randomly-selected trip from U_d will lead to a measured exposure of c or more on the dth day
M:	the total number of days in D
L_{ud}:	the number of replicates measured for the uth trip on the dth day (i.e., L_{ud} samplers in one vehicle)
g_{ju}:	unbiasing constant used to estimate $\bar{F}_{jz}(c\|d)$. In Section 3, this is the number of feasible sequences, s, that contain the trip u in the jth stratum.
$p_j(s_k)$:	probability of choosing the sequence s_k in the jth stratum
^:	hats over symbols (e.g., $\hat{\bar{F}}$) represent estimators of the entities under the hats

m_j: number of days sampled in D for which data were taken in the jth stratum

$m_{jj'}$: number of days sampled in D for which data were taken in both the jth and j'th stratum

λ_j: proportion of trips in the jth stratum

j: index indicating the jth stratum in a set of trips

U: the set of all trips in D. $U = \bigcup_{d \epsilon D} U_d$

$\bar{F}_{jz}(c|d)$: probability that a randomly-selected trip from the jth stratum will lead to a measured exposure of c or more on the dth day

K_{dj}: the number of pairs of cars sampling from the jth stratum on the dth day

k: index indicating a specific pair of cars

$z_{ud\ell}$: the ℓth replicate of the measured exposure for the uth trip on the dth day

$z_{ud.}$: the average over L_{ud} replicates of the $z_{ud\ell}$

U_j: set of trips over all D in the jth stratum

N_j: number of trips in U_j

J: number of strata

K_{ij}: number of cars sent into the jth stratum using allocation t_i

t_i: ith allocation of cars among the J strata. $t_i = (K_{i1},\ldots,K_{iJ})$

v_i: number of days for which allocation type t_i is used

S_j: set of sequences of trips in the jth stratum constructed so that they can be feasibly taken by one car in one day

R: number of allocation types, t_i

$\beta(u,s_k)$: coefficients used to estimate the probability that a randomly-selected trip will yield an exposure greater than c for a given day based on data taken by one vehicle

$r(s)$: arbitrary coefficients that can be applied to each sequence s in S to affect the relative frequency that that sequence will be sampled

$g(u), g_u$: number of sequences (weighted by $r(s)$) that the trip u is in

$w_j(d)$: proportion of trips in the jth stratum relative to the total number of trips in the trip population on the dth day

$\hat{w}_j(d)$: estimate of $w_j(d)$

$h(q_j)$: probability of choosing the set of days q_j from D

q_j: the set of days $(d_1,\ldots,d_{m_j})$ sampled for which data are taken from the jth stratum

APPENDIX

RELATION BETWEEN $\bar{F}_y$ and $\bar{F}_z$

As a first approximation, assume the ℓth replicate measurement for the uth trip taken on day d has the form

$$z_{ud\ell} = a_{(ud)\ell} y_{ud} + b_{(ud)\ell}$$

where a and b given the trip u are independent random variables (errors) with expectation one and zero, respectively, and variances σ_a^2 and σ_b^2. The variate y_{ud} represents the true exposure for the uth trip on the dth day. The purpose of the following is to see what biases are introduced into the analysis by using $\bar{\bar{F}}_z$ as an approximation to $\bar{\bar{F}}_y$.

Let

$$z_{ud.} = \sum_{\ell=1}^{L_{ud}} z_{ud\ell}/L_{ud}$$

$$= a_{ud.} y_{ud} + b_{ud.} \qquad \text{(A.1)}$$

Let dH(a,b,u,d) be the joint probability density of a, b, y and d. If a and b are independent unconditionally and do not depend upon u and d, then $H(a,b,u,d) = dH_1(a,b)dH_2(u,d)$. The following equality for the unconditional probability that $z_{ud.}$ is greater than c results.

$$\bar{F}_z(c) = P\left\{z_{ud.} > c\right\}$$

$$= \int_a \int_b P\left\{y_{ud} > (c-b)/a \,|\, a,b\right\} dH_1(a,b)$$

$$= \iint_{a,b} \bar{F}_y\left(\frac{c-b}{a}\right) dH_1(a,b) \qquad \text{(A.2)}$$

If the variances of a and b are small relative to the value of c under consideration, we can expand $\bar{F}_y((c-a)/b)$ in a Taylor's series about a = 1 and b = 0. Performing such a procedure, we obtain

$$\bar{F}_z(c) = \bar{F}_y(c) + \sigma_a^2/2L \left\{ c^2 \left. \frac{d^2\bar{F}_y(x)}{dx^2} \right|_{x=c} + 2c \left. \frac{d\bar{F}_y(x)}{dx} \right|_{x=c} \right\} + \sigma_b^2/2L \left\{ \left. \frac{d^2\bar{F}_y}{dx^2} \right|_{x=c} \right\} \qquad \text{(A.3)}$$

Consider the case in which $\bar{F}_y(c)$ is essentially exponential in a neighborhood of c. That is, $\bar{F}_y(c) \simeq \exp(-\lambda c)$. (The form that Horowitz and Papetti [1975] found in their analysis looks very close to an exponential function in c.) With this assumption, we see that

$$\bar{F}_{z.}(c) = \bar{F}_y(c)\left\{1 + \frac{\sigma_a^2}{2L}\left[(\ln\bar{F}_y(c))^2 + 2\ln\bar{F}_y(c)\right] + \sigma_b^2/(2L\sigma_{TOT}^2)\right\} \tag{A.4}$$

where σ_{TOT}^2 is the total variance of y $(1/\lambda^2)$. Horowitz and Papetti's work indicates $\lambda = 0.5$ m^3/μg. A typical analytical error bound might be

$$|\text{analytical error}| \leqslant 0.3 + 0.25[H_2SO_4] \tag{A.5}$$

This implies $2\sigma_b = 0.3$ and $2\sigma_a = 0.25$. Then

$$\bar{F}_z(c) = \bar{F}_y(c)\left\{1 + \frac{0.0078}{L}\left[+ 2\ln\bar{F} + (\ln\bar{F})^2\right] + 0.0028/L\right\}. \tag{A.6}$$

At the 90th percentile of $\bar{F}_y(c)$, $(\bar{F}_y(c) = 0.1)$, we have

$$\bar{F}_z(c) = 0.1[1 + 0.008/L] \tag{A.7}$$

Thus, only an 0.8% bias is introduced into the estimate with one replicate when the initial error is less than 0.3 μg/m^3 plus 25% of reading.

One might define the average squared error patterned after the Cramér-Von Mises statistic:

$$\bar{E}^2 = \int_c \left(\bar{F}_z(c) - \bar{F}_y(c)\right)^2 dF_y(c) \tag{A.8}$$

For $\bar{F}_y(c) \simeq \exp(-\lambda c)$,

$$\bar{E}^2 = \Big[56(\sigma_a^2/2L)^2 + 48(\sigma_a^2/2L)(\sigma_b^2/2L\sigma_{TOT}^2) + 27(\sigma_b^2/2L\sigma_{TOT}^2)^2\Big]\Big/81 \tag{A.9}$$

For the estimated values $\sigma_a = 0.125$, $\sigma_b = 0.15$, $\sigma_{TOT} = 1/\lambda = 2.0$, we have

$$\bar{E} = 0.0076 \tag{A.10}$$

for L = 1. Thus, the average error is less than 1%.

A statistic which gives higher weight to the right-hand tail of the distribution (where decision on control strategy will be based), can be patterned after the Anderson-Darling goodness-of-fit criteria. This gives

$$E_W^2 = \int_0^\infty \Big[\left(\bar{F}_z(c) - \bar{F}_y(c)\right)/\left(\bar{F}_y(c)\right)^{1/2}\Big]^2 dF_y(c) \tag{A.11}$$

Again assuming $\bar{F}_y(c) \simeq \exp(-\lambda c)$, we have

$$\bar{E}_w^2 = \frac{1}{4}\left[13(\sigma_a^2/2L)^2 + 4(\sigma_a^2/2L)(\sigma_b^2/2L\sigma_{TOT}^2) + 2(\sigma_b^2/2L\sigma_{TOT}^2)^2\right] \qquad (A.12)$$

For the same estimated error values as above, we obtain $\bar{E}_w = 0.0150$ with only one replicate.